

# Thermionic Emission Measurements of 12(CaO)-7(Al<sub>2</sub>O<sub>3</sub>) Electride in a Close-Spaced Diode

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**Many electric propulsion devices use a thermionic cathode as a source of free electrons for plasma ignition or maintaining charge neutrality in the exhaust plume. Popular cathode insert materials require high operating temperatures and/or high purity propellants to maintain a low work function. Preliminary results of thermionic emission from 12(CaO)-7(Al<sub>2</sub>O<sub>3</sub>) (C12A7) samples promise a low temperature electron emitter with resistance to poisoning but work function estimates vary greatly and poisoning behavior is anecdotal. This study experimentally measures the thermionic emission of a planar disc sample of C12A7 electrified in a close-spaced diode under vacuum at  $3.5 \times 10^{-8}$  Torr for sample temperatures of 690/700, 850, 980, 1096, and 1200°C. Changes in thermionic emission current density for sample annealing at 700°C (24 and 44 hour long durations) and 980°C (1 and 24 hour long durations) are also presented. Overall, thermionic emission is found to decrease in magnitude with increasing annealing duration times across most cathode temperature conditions considered.**

## I. Introduction

CATHODE structure, materials, and configuration often determine the life expectancy and performance of electric propulsion devices requiring a source of free electrons.<sup>1</sup> Thermionic cathodes require an active electron emitter with a low work function surface such as barium impregnated porous tungsten (Ba-W) with a work function of 2.1 eV or Lanthanum hexaboride (LaB<sub>6</sub>) with a work function of 2.7 eV.<sup>2</sup> Unfortunately, emission from a Ba-W insert relies on the material's surface chemistry making it highly susceptible to poisoning by oxygen and water vapor. A popular alternative to Ba-W inserts are LaB<sub>6</sub> inserts considered resistant to contamination by oxygen and water vapor but which require a high operating temperature of approximately 1600°C. In addition, neither Ba-W or LaB<sub>6</sub> are suitable materials for cathode operation on iodine,<sup>2</sup> an attractive propellant for electric propulsion devices due to its high density and low ionization threshold.

A calcium-aluminate electrified 12(CaO)-7(Al<sub>2</sub>O<sub>3</sub>) or C12A7 characterized as a thermally and chemically stable electrified capable of low temperature electron emission<sup>3</sup> has attracted attention as an alternative to traditional emitter materials.<sup>2,4-5</sup> Unfortunately, field emission measurements corresponding to a work function of 0.6 eV differ wildly from ultra-violet photoelectron spectroscopy (UPS) and other material property diagnostics resulting in work function estimates ranging from 2.4 to 3.7 eV.<sup>6-7</sup> Despite differing work function estimates, implementation of a C12A7 insert into a hollow cathode assembly has led to successful ignition without external heating and operation on both xenon and iodine.<sup>2</sup> While consistent emission behavior in the cathode assembly was achieved, multiple processing runs on xenon totaling several tens of hours and a change in cathode operating temperature of ~230°C were required. Causes of the inconsistent emission behavior of C12A7 are unclear.

Inconsistent emission behavior observed during testing of samples of C12A7 may result from the different material processes used to form the electrified. Fabrication methods for C12A7 vary in temperature, duration of heating,

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procedure (sintering, melting, etc.), method of oxygen extraction, and quenching temperature which may contribute to the differences observed in material work function.<sup>2,5,8</sup> Sensitivity to manufacturing processes was highlighted in a study of surface treatments of C12A7 electride by Toda.<sup>9</sup> Removal of the O<sup>2-</sup> ion from C12A7 crystal structure cages leaves behind an electrically insulating oxide layer that increases the material work function. Removal of this layer via ion bombardment or mechanical abrasion can damage the outer cages also increasing the material work function. Annealing the electride following removal of the oxide layer precipitates crystal growth restoring C12A7's low work function on subsequent emission tests. Overall, a better understanding of how fabrication procedures influence emission characteristics of C12A7 is required to select electride samples best suited for thermionic cathode operation. In addition, evaluation of electride handling techniques used to regrow/maintain the crystal structure cages required for low-temperature electron emission following different methods of O<sup>2-</sup> extraction would be beneficial.

Another quality of C12A7 that has attracted attention is its supposed resistance to poisoning, however, observations regarding this behavior remain anecdotal.<sup>2,5</sup> Gallagher's<sup>10</sup> evaluation of LaB6 cathode poisoning resistance included a measure of thermionic emission current at standard electride operating temperatures in the presence of varying partial pressures of oxygen and other contaminating gases. Emission current collected in the presence of contaminating species was compared to emission current collected under ideal cathode conditions to determine the poisoning gas partial pressure operating limits of LaB6. This evaluation provides a comparison of LaB6 emission behavior in the presence of a contaminating species with the performance of other cathode materials including Ba-W under similar environmental conditions.

The range of work function estimates for C12A7 has precipitated a need to develop a method of measuring the thermionic emission of C12A7 produced via different fabrication methods at various temperatures and following a range of post fabrication treatments. The ability to introduce oxygen and water vapor during thermionic emission measurements of C12A7 is also desirable. This work focuses on the development of a close-spaced diode capable of heating planar samples of electride material and measuring the resulting thermionic emission. The parallel plane diode architecture is chosen in order to enable determination of the material work function from the sample emission current density using a combined model for thermionic Richardson-Dushman Emission and Schottky-enhanced high voltage emission developed by J.B. Scott.<sup>11</sup> At time of publication, a MatLab code using the J.B. Scott model is still in development. Validation of the close-spaced diode concept is presented here using C12A7 sample thermionic emission current density measurements recorded at a background operating pressure of  $3.5 \times 10^{-8}$  Torr for sample temperatures of 690/700, 850, 980, 1096, and 1200°C. In addition, thermionic emission current density changes following sample annealing at 700°C and 980°C are also presented.

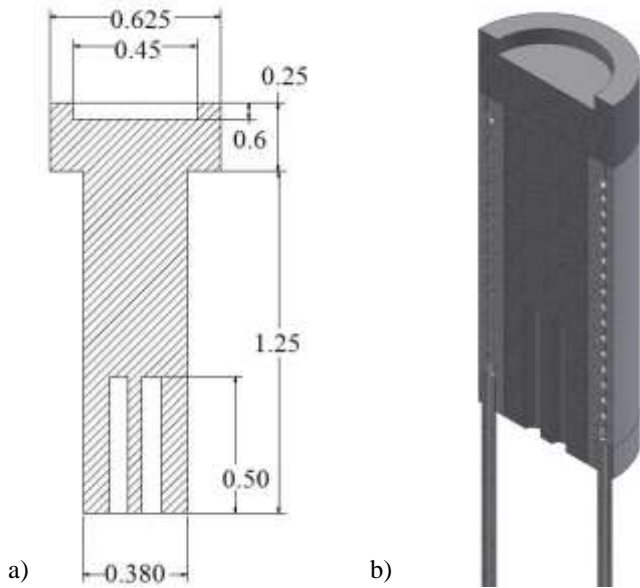
## II. Experimental Setup

### A. Close-Spaced Diode

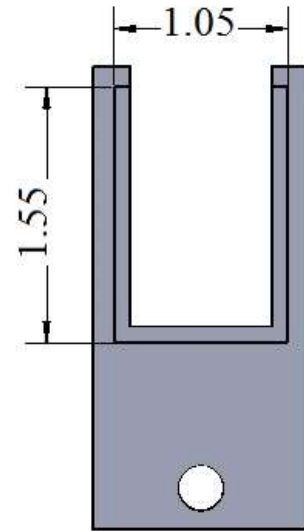
Sample emission current is collected in a custom built, close-spaced diode. The cathode portion of the assembly which holds the C12A7 emitter is comprised of a rhenium hollow cathode heater and a solid molybdenum sample cup wrapped in molybdenum foil and mounted using alumina tubing. The heater is a double-helical rhenium heater filament wound around a hot-pressed boron nitride cylinder as shown in Fig. 1. The heater filament is then fully encased inside a concentric boron nitride sleeve as detailed in Ref. 12. The molybdenum sample cup shown in Fig 2a. slides into the rhenium hollow cathode heater as shown in Fig. 2b and is heated via conduction through the surrounding boron nitride cylinder. The sample cup inset can accommodate disc-shaped emitter samples up to 0.45 inches in diameter and 0.06 inches thick. The outer surface of the sample cup has been polished. The entire assembly is wrapped in 3N8 purity molybdenum foil, 0.001 inches thick, to reduce thermal losses by lowering the assembly's thermal emissivity. The molybdenum foil is held in place via friction using twisted molybdenum wire around the outer circumference of the assembly. The molybdenum sample cup, C12A7 emitter, and molybdenum foil are grounded. The rhenium heater filament is powered by a Keysight N5771A 300V, 5A DC power supply and remains electrically floating during operation.



**Figure 1. Double-helical rhenium heater filament wrapped around boron nitride cylinder. Heater shown above is installed in a hollow cathode assembly with the exterior sleeve removed.**



**Figure 2. a) Cross section of molybdenum sample cup; dimensions in inches. b) Cross section of molybdenum sample cup mounted in rhenium hollow cathode heater.**



**Figure 3. Stainless steel anode holder can accommodate anode sizes up to 1.05 inches wide and 1.55 inches long.**



**Figure 4. Complete close-spaced diode assembly operating at 980°C cathode temperature with a C12A7 emitter sample. The entire assembly runs inside the Plasma Test Facility.**

The anode is supported by an electrically grounded, stainless steel, threaded rod. Electrical isolation is provided by a ceramic standoff at the top of the support structure. A stainless steel anode holder, shown in Fig. 3, holds a removable anode parallel to the top plane of the cathode assembly. Due to the electrical isolation provided by the ceramic standoff only the anode and anode holder have a positive voltage. For this work, molybdenum foil is used as the anode material.

The anode holder and molybdenum foil anode are biased using a Keithley 2450 Sourcemeter via a ring terminal connection at the top of the anode assembly. For all data presented, the anode is swept from 0-210V relative to chamber ground. Current is recorded every 5V with a 10 ms dwell time at each voltage condition and a 10 s dwell time at the start of each sweep. Current is recorded three times at each voltage condition and averaged to yield the final data point for each emission current trace. A minimum of three traces are recorded for each cathode temperature of interest for the C12A7 emission data presented. Traces are recorded using a custom build LabView VI. Figure 4 shows the close-spaced diode in operation at the 980°C cathode temperature condition.

Preliminary sample cup temperatures were recorded using a 0.010-inch diameter k-type

thermocouple imbedded in the sample cup until failure at 1000°C. For measurements above 1000°C, sample cup temperature is determined using a logarithmic curve fit to the previously recorded temperatures for a given rhenium heater operating current. Temperature measurements are recorded using a Measurement Computing E-TC multichannel thermocouple reader.

## B. Plasma Test Facility

The close-spaced diode is mounted on a stainless steel optical breadboard placed inside the Plasma Test Facility (PTF) at the United States Naval Research Laboratory (NRL). The PTF is a cylindrical stainless steel vacuum chamber measuring 39 inches long and 30 inches in diameter.

A Varian TriScroll 600 dry scroll pump backs an Agilent Turbo-V 10001 Navigator turbopump mounted at the top of the chamber with a nominal 950 L/s pumping speed on air. A CTI Cryo-Torr 400 cryopump mounted on the bottom of the chamber provides an additional, nominal 6000 L/s pumping speed on air. A Lesker 392 series hot ionization gauge monitors high vacuum pressure. Both vacuum pumps are engaged for this work yielding an operating pressure of approximately  $3.5 \times 10^{-8}$  Torr.

## III. Results

### A. Preliminary Sample Assessment

The C12A7 sample characterized in this work is one of ten discs purchased via Dr. Martin Tajmar of Technische Universität Dresden and produced in collaboration between Dr. Tajmar and Fraunhofer IKTS. All discs measure 11 mm in diameter and 1 mm thick. The material was formed initially from a rapidly quenched C12A7 melt. The resulting glass was milled to powder, pressed into a green shape for machining, and finally sintered in a reducing environment.

In order to catalogue any phase or chemical composition changes induced in the sample during emission testing, X-ray diffraction (XRD), 4-point probe conductivity, and 200x magnification photographic analyses are completed on the chosen sample, Sample-6. Prior to testing the C12A7 sample in the close-spaced diode, XRD analysis confirms the sample material tested is in the C12A7 material phase. 4-point probe conductivity measurements estimate the resistance of Sample-6 to be  $\sim 2760 \text{ M}\Omega/\text{square} \pm 260 \text{ M}\Omega/\text{square}$ . The sample characterized was chosen out of the 10 total samples for its uniform color and relatively smooth appearance as observed at 200x magnification as shown in Fig. 5.

Prior to emission current density measurements, the sample was dry-polished at NRL using fine grit, silicon carbide sandpaper. In addition, the sample face in contact with the molybdenum sample cup was plated in an evaporated refractory metal coating to provide electrical contact with the sample cup.

### B. Thermionic Emission Results

Initial emission current is collected for cathode temperatures of 690, 850, 980, 1096, and 1200°C across an anode bias ranging from 0-210V. The sample is allowed 30 minutes at each heater operating condition (corresponding to a particular cathode temperature) to thermally equilibrate before emission measurements are recorded. Immediately following emission current collection at the 1200°C cathode temperature, the rhenium heater power is reduced to the 700°C operating condition and the sample is annealed for 24 hours. At the 24-hour mark, emission current is collected for cathode temperatures of 700, 850, and 980°C. Note, the 690°C operating condition recorded previously was due to a slower than predicted approach to thermal equilibrium at the same heater operating power as the 700°C operating condition. Due to emission current changes observed at the 700°C cathode temperature, an additional anneal at 700°C is conducted. Heater power was again reduced to the 700°C operating condition following emission data collection at the 980°C cathode temperature and the sample was annealed for an additional 20 hours. After a total of 44 hours from the initial start of the 700°C anneal, emission current was again recorded at the 700, 850, and 980°C cathode temperatures. Following collection at the 980°C cathode temperature, the rhenium heater maintained the 980°C cathode temperature and emission measurements are recorded at the 1-hour and 24-hour marks. 980°C is chosen for the final anneal due to existing literature cataloguing the temperature range of 950-1000°C as the C12A7 recrystallization temperature over which the damaged cage structure of C12A7 can be repaired<sup>13</sup> and emission is expected to improve.



**Figure 5. C12A7 Sample-6 photographed at 200x magnification.**

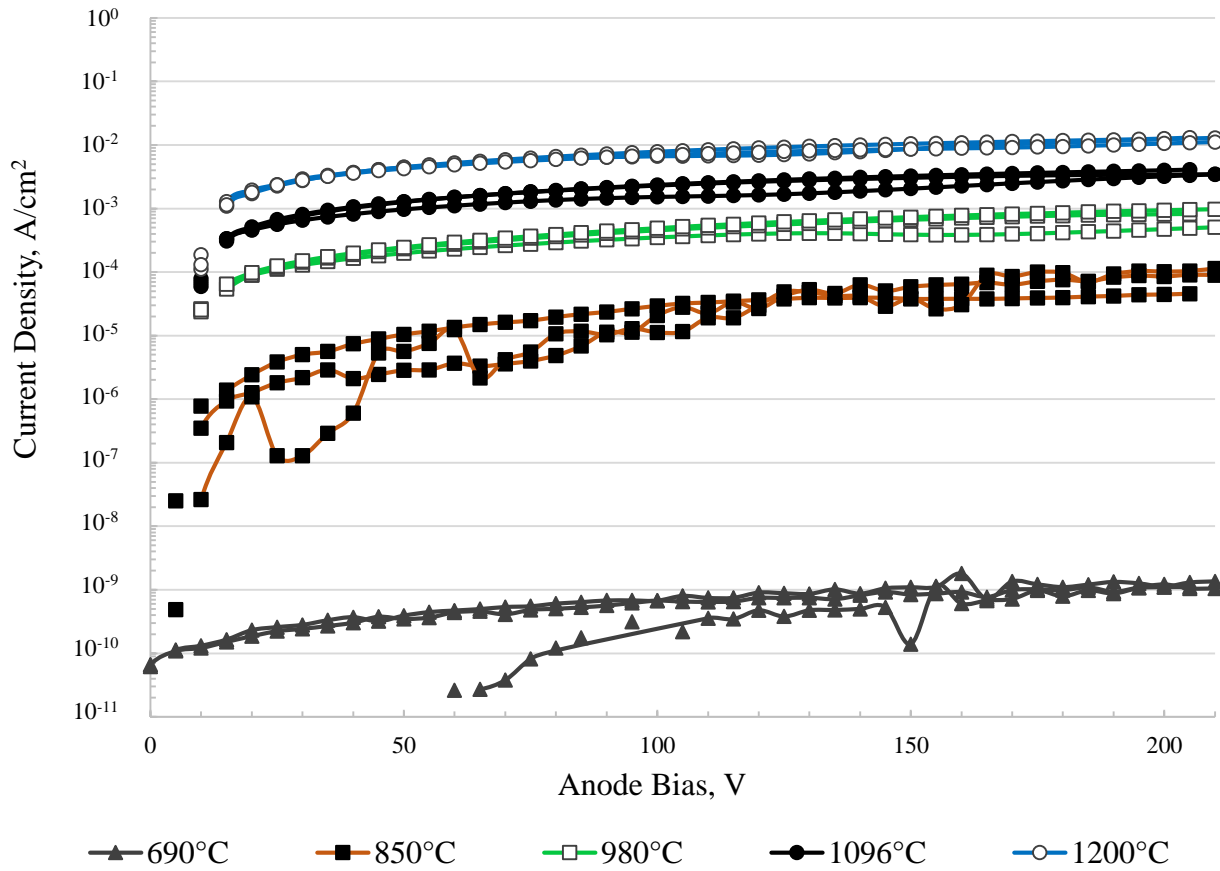


Figure 6. Initial emission current density measurements of C12A7 Sample-6 for cathode temperatures ranging from 690°C to 1200°C across an anode bias range of 0-210V.

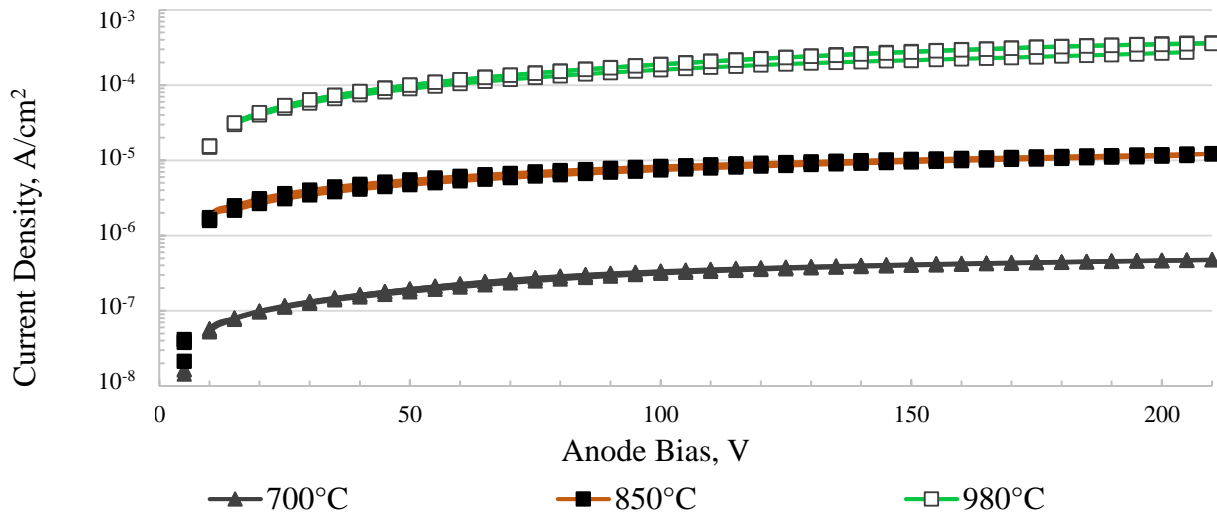


Figure 7. Emission current density measurements following a 24 hour long anneal at 700°C of C12A7 Sample-6 for cathode temperatures ranging from 700°C to 980°C across an anode bias range of 0-210V.

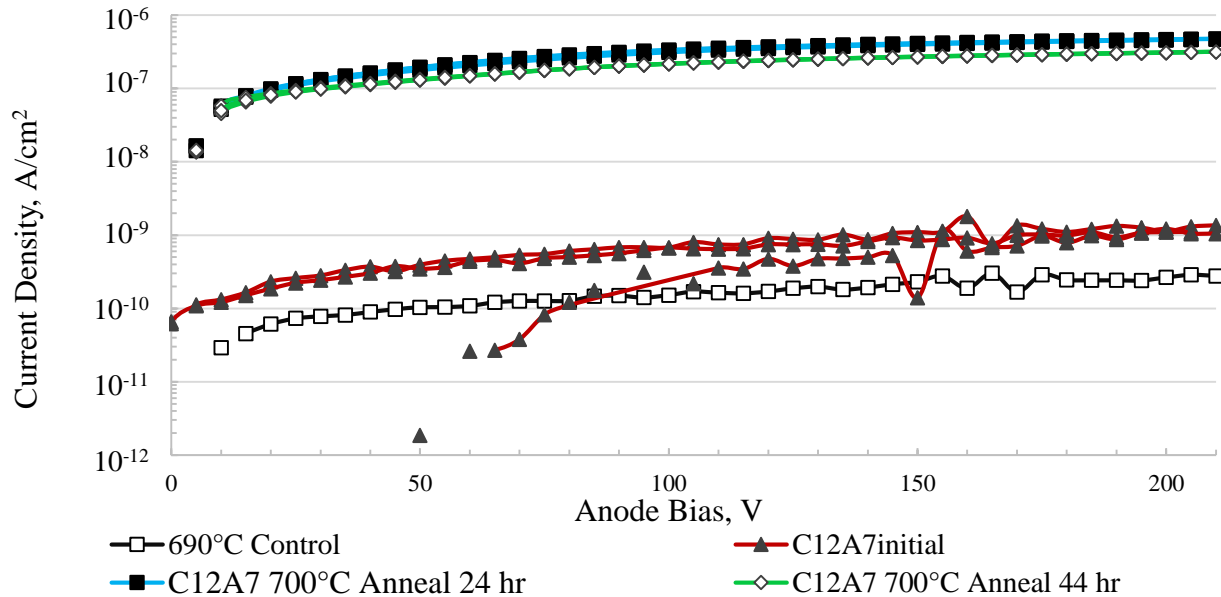
Surface sputtering of the C12A7 surface, as recommended by Ref. 9 to clean the sample surface of oxide layers is attempted but plasma density generated in the close-spaced diode was insufficient. 50 sccm of argon entered the PTF while the cathode temperature remained at 980°C and a 200V bias was maintained on the anode. Emission measurements recorded during the process (not presented here) showed no evidence of oxide layer cleaning.

Initial emission current density measurements for C12A7 Sample-6 are shown in Fig. 6. Emission current density increases with increasing cathode temperature by roughly an order of magnitude per 100°C for cathode temperatures  $\geq 850^\circ\text{C}$  at the 210V anode bias. Emission measurements decrease in noise at higher temperatures yielding smaller deviations in current collected at each anode voltage condition for a given cathode temperature.

Immediately following data collection at the 1200°C cathode temperature, the sample was annealed for 24 hours at 700°C. Emission current density measurements for 700, 850, and 980°C cathode temperature following the 24-hour anneal are shown in Fig. 7. Both the 700°C and the 850°C cathode temperature cases show a reduction in noise and decreased deviation in current collected at each anode voltage condition for a given cathode temperature. Current density for the 700°C condition increased over two orders of magnitude at an anode bias of 210V to  $4.7 \times 10^{-7}$  A/cm<sup>2</sup> from  $1.0 \times 10^{-9}$  A/cm<sup>2</sup> at the 690°C cathode temperature prior to the anneal. In contrast, both the 850°C and 980°C cathode temperature conditions reduced in maximum current density at the 210V anode bias by  $9.8 \times 10^{-5}$  A/cm<sup>2</sup> and  $1.5 \times 10^{-4}$  A/cm<sup>2</sup> respectively.

Following emission current density measurements at 980°C, cathode temperature was reduced to 700°C for an additional 20 hours. Emission current density is again recorded after a total of 44 hours at 700°C or above, due to emission testing at higher cathode temperatures discussed earlier during the anneal, for the 700°C, 850°C, and 980°C cathode temperatures. Emission data are plotted against the previous two emission traces at each cathode temperature in Fig. 8-10. Also shown on the individual cathode temperature plots are control sweeps for each cathode temperature recorded for the close-spaced diode operating in vacuum without an emitter sample present. All emission current density measurements for C12A7 are greater than the control emission sweeps with the exception of one of the first sweeps recorded at the 690°C shown in Fig. 8.

Emission current density measurements, shown in Fig. 8, at the 700°C cathode temperature following the 44-hour 700°C anneal show a reduction in current density of  $3.0 \times 10^{-9}$  A/cm<sup>2</sup> at the 5V anode bias up to a  $1.5 \times 10^{-7}$  A/cm<sup>2</sup> decrease at the 210V anode bias. At the 850°C cathode temperature shown in Fig. 9, there is no discernible difference in the magnitude of emission current density collected between the 44-hour and 24-hour anneals until an anode bias of 165V is reached after which the 44-hour anneal emission current exceeds the 24-hour anneal in magnitude. Figure 10 shows the results of the 44-hour 700°C anneal for the 980°C cathode temperature. There are no discernible changes in emission current density between the 24-hour and 44-hour 700°C anneal for the 980°C cathode temperature.



**Figure 8. Comparison of emission current density measurements at 700°C cathode temperature following 24 and 44-hour long anneals at 700°C for an anode bias range of 0-210V. The control curve represents emission recorded in the close-spaced diode in the absence of an emitter sample at 690°C cathode temperature.**

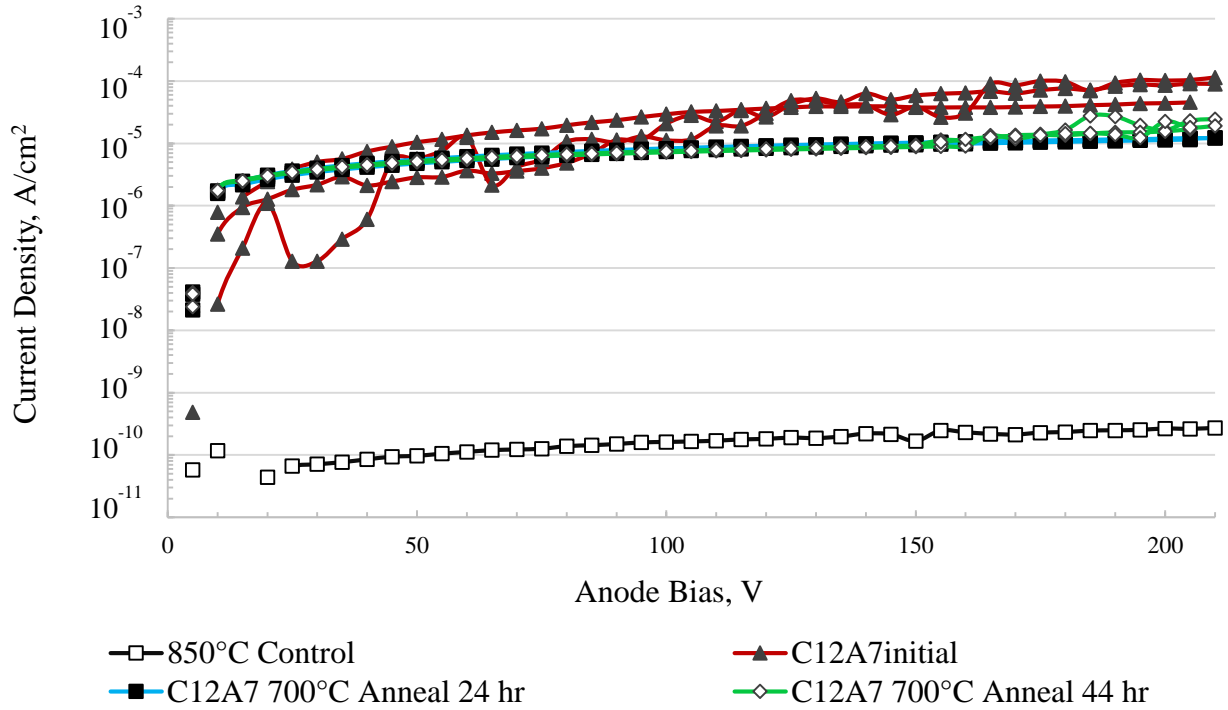


Figure 9. Comparison of emission current density measurements at 850°C cathode temperature following 24 and 44-hour long anneals at 700°C for an anode bias range of 0-210V. The control curve represents emission recorded in the close-spaced diode in the absence of an emitter sample at 850°C cathode temperature.

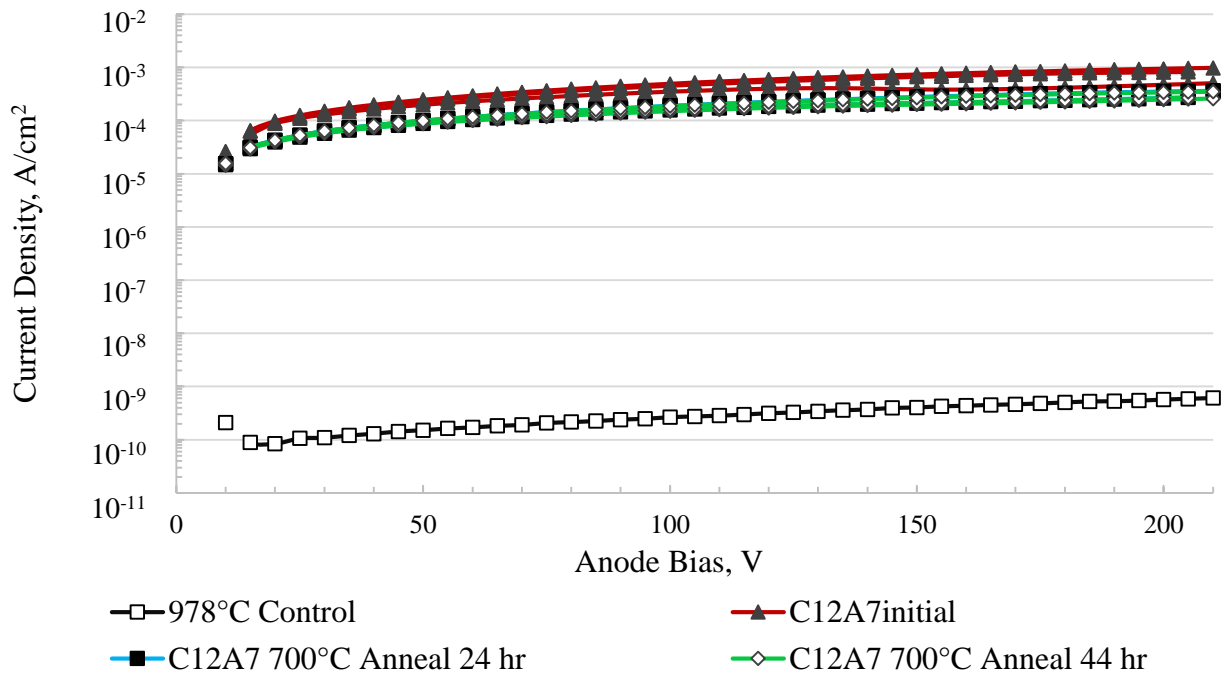
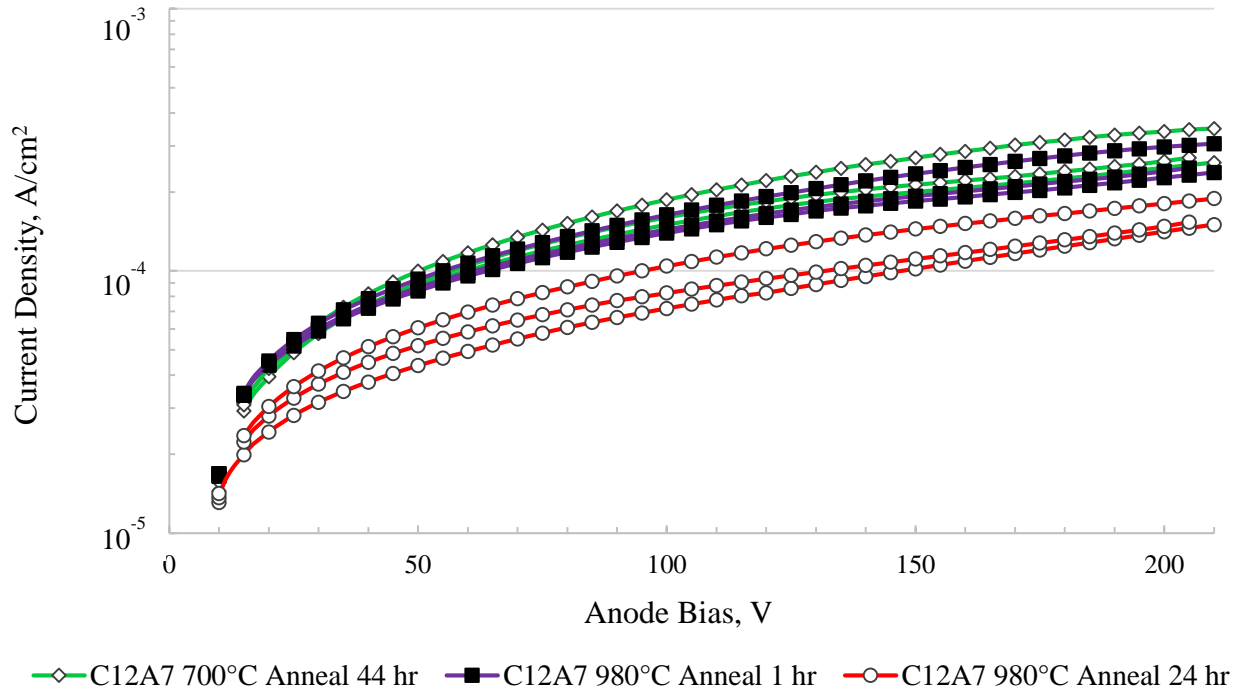


Figure 10. Comparison of emission current density measurements at 980°C cathode temperature following 24 and 44-hour long anneals at 700°C for an anode bias range of 0-210V. The control curve represents emission recorded in the close-spaced diode in the absence of an emitter sample at 980°C cathode temperature.



**Figure 11. Comparison of emission current density measurements at 980°C cathode temperature following 1 and 24-hour long anneals at 980°C for an anode bias of 0-210V. The 980°C anneal occurs after the 44-hour anneal at 700°C for C12A7 Sample-6.**

Following completion of the emission data collection at the 980°C cathode temperature for the 44-hour, 700°C anneal, the sample underwent an ineffective sputtering attempt at 980°C followed by an additional hour long anneal at 980°C. Emission current density measurements for C12A7 Sample-6 at the 980°C cathode temperature following the 1-hour anneal are  $3.0 \times 10^{-6}$  A/cm<sup>2</sup> greater at the 10V anode bias but  $4.0 \times 10^{-5}$  A/cm<sup>2</sup> less at the 210V anode bias. Following an additional 23 hours at 980°C, sample emission current density drops across the full anode voltage range considered as shown in Fig. 11. After the 24-hour long anneal, the sample's thermionic emission current is reduced by  $1.0 \times 10^{-5}$  A/cm<sup>2</sup> at the 10V anode bias and  $1.6 \times 10^{-4}$  A/cm<sup>2</sup> at the 210V anode bias from performance observed prior to either 980°C anneal. Following data collection at the 980°C cathode temperature after the 24-hour 980°C anneal, the test is complete and the assembly is fully cooled to the ambient laboratory temperature at vacuum.

## IV. Discussion

### A. Close-Spaced Diode Performance

The close-spaced diode assembly presented in this work successfully heats a planar disc sample of C12A7 electride and collects thermionic emission current for cathode temperatures of 690/700, 850, 980, 1096, and 1200°C. Emission collection in the close-spaced diode is consistent, varying marginally at individual anode voltages for a given test condition (cathode temperature and sample treatment). Control emission curves recorded for an empty diode assembly remain significantly lower than emission curves recorded in the presence of a C12A7 sample indicating the assembly orientation and material selection are suitable for thermionic emission characterization.

The goal of building a parallel plane diode capable of collecting thermionic emission current from planar samples of C12A7 electride is accomplished in the close-spaced diode design. In addition, annealing samples at a given cathode temperature is also possible in the close-spaced diode presented. Future modifications to the assembly to allow real time temperature measurements by implementing an R-type thermocouple and/or using an ITO coated quartz slide instead of molybdenum foil for the anode (enabling pyrometer measurements with direct line of sight of the heated sample) are planned. Other modifications of interest include real time resistance measurements of heated samples (see Section IV.C) and an argon sputtering assembly (see Section IV.C).



## B. Thermionic Emission at the 700°C Cathode Temperature

Following the 700°C 24-hour anneal, thermionic emission current recorded at the 700°C cathode temperature rises over two orders of magnitude at the 210V anode bias and the entire curve exhibits a great reduction in noise. Currently, it is unclear the cause of the emission magnitude increase and reduction in noise. Since thermionic emission measurements at the 700°C cathode temperature are not repeated directly following emission measurements at 1200°C, it is not known if the 24-hour anneal or the heating of the sample required to take the emission current measurements at cathode temperatures above 700°C yielded in the observed changes. Future tests will implement a cool down step following the final cathode temperature operating condition to record a second round of 'initial' thermionic emission values prior to performing any post fabrication treatments in the vacuum chamber to determine if the cause(s) of the observed changes in thermionic emission shown in this work are due to the release of adsorbed gases in the sample or diode assembly or a result of material changes in the electride following an anneal.

## C. Thermionic Emission as a Function of Anneal Duration

With the exception of the 24-hour, 700°C anneal results at the 700°C cathode temperature discussed in Section IV.B, all other cathode temperatures exhibit either decreased thermionic emission or negligible changes in thermionic emission with increasing duration of post fabrication annealing at either 700°C or 980°C. The absence of changes in thermionic emission values may result from either insufficient oxide layer removal during the dry polishing process described in Section III.A or results from poisoning of the C12A7 sample by either diatomic oxygen or water vapor due to damaged surface cages resulting from the polishing process.<sup>9</sup> In either case, in-vacuum oxide layer removal via argon ion sputtering is required to sufficiently remove existing oxide layers following fabrication, to prevent oxide layers from reforming at atmosphere prior to placing the sample in the close-spaced diode, and to prevent sample poisoning by diatomic oxygen or water vapor prior to repairing the poisoning-resistant surface cages of C12A7 with a post-sputtering anneal.

Thermionic emission sweeps that showed decreasing emission magnitude may result from any of the following causes: C12A7 phase transition, poisoning due to mid-level vacuum operation, calcium depletion, increased sample resistance, or changes in the close-spaced diode's anode assembly. The first possible source of decreased thermionic emission may be due to a shift out of the C12A7 phase of the material into one of its less emissive phases. A pending XRD analysis of Sample-6 will indicate if a phase change has occurred.

The second reason for reduced emission listed above, may be due to the operating pressure of the PTF during sample heating and annealing. C12A7 electride is stable in air up to 400°C<sup>14</sup> but it is unclear how stability relates to increasing temperature at various levels of vacuum. Operation at 10<sup>-8</sup> Torr may poison the C12A7 sample with the remaining oxygen and water vapor circulating inside the chamber resulting in reduced thermionic emission. Higher vacuum levels may be required for successful operation of the close-spaced diode.

Another sample material modification that may result in reduced thermionic emission is depletion of calcium from the surface due to extended heating durations. Calcium depletion was previously observed to be a concern at annealing temperatures above 1050°C<sup>9</sup> which makes its applicability in this instance unlikely. However, previous anneal durations that exhibited calcium depletion in C12A7 at temperatures above 1050°C were only an hour long in duration<sup>9</sup> and it is unclear if extended annealing at lower annealing temperatures would yield similar results. 200x magnification on the sample surface to identify gray patches indicative of calcium depletion<sup>9</sup> will identify surface areas that are good candidates for X-ray photoelectron spectroscopy (XPS) which will identify changes in chemical composition (such as reduced calcium) from XPS measurements recorded prior to sample testing.

Another source of reduced thermionic emission may be a result of increased sample resistance. Increasing sample resistance will alter the electric field generated in the close-spaced diode in addition to limiting the total current that can be emitted from the sample at a given operating condition. The cause of increasing sample resistance is currently unknown but 4-point probe measurements are scheduled to determine if a change in the material bulk resistance of ~2760 MΩ/square ± 260 MΩ/square measured prior to sample testing has occurred.

The final cause considered for the observed reduction in thermionic emission current with increasing duration of sample annealing involves the close-spaced diode assembly itself. While control sweeps yielded emission measurements significantly lower than those observed during operation with C12A7, successive control sweeps following sustained temperatures at vacuum were not recorded. Examination of the anode material for deformation during operation as well as additional control sweeps following long heating durations may be necessary to eliminate the close-spaced diode as a cause of the observed emission behavior changes.

## V. Conclusion

Previous studies of C12A7 material yield promising but conflicting estimates of material work function. In order to allow computation of the work function from thermionic emission curves, a parallel plane, close-spaced diode is designed to heat and anneal planar emitter samples as well as collect thermionic emission current for analysis. The close-spaced diode presented in this work shows promising initial results as a viable means of characterizing C12A7 thermionic emission behavior following further investigation into the cause(s) of changes in emission behavior during post-fabrication processes such as the 700°C and 980°C anneals. Changes in experimental procedure such as additional assembly cool down events are also planned to better isolate the sources of sample emission improvement.

## Acknowledgments

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## References

- <sup>1</sup>Goebel, D. M., and Katz, I., *Fundamentals of Electric Propulsion: Ion and Hall Thrusters*, John Wiley & Sons, Inc., Hoboken, 2008, Chap. 6.
- <sup>2</sup>Rand, L. P., and Williams, J. D., "A Calcium Aluminate Electride Hollow Cathode," *IEEE Transactions on Plasma Science*, Vol. 43, No. 1, 2014, pp. 190-194.
- <sup>3</sup>Matsuishi, S., Toda, Y., Miyakawa, M., Hayashi, K., Kamiya, T., Hirano, M., Tanaka, I., and Hosono, H., "High-Density Electron Anions in a Nanoporous Single Crystal:  $[\text{Ca}_{24}\text{Al}_{28}\text{O}_{64}]^{4+}(4e^-)$ ," *Science*, Vol 301, No. 5633, 2003, pp. 626-629.
- <sup>4</sup>Rand, L. P., "A Calcium Aluminate Electride Hollow Cathode," Ph.D. Dissertation, Dept. of Mechanical Engineering, Colorado State Univ., Fort Collins, Co, 2014.
- <sup>5</sup>Drobny, C., Nürmberger, F., and Tajmar, M., "Development of a Compact Hall Thruster with a C12A7 Low-Power Hollow Cathode," 2016.
- <sup>6</sup>Toda, Y., Matsuishi, S., Hayashi, K., Ueda, K., Kamiya, T., Hirano, M., Hosono, H., "Field Emission of Electron Anions Clathrated in Subnanometer-Sized Cages in  $[\text{Ca}_{24}\text{Al}_{28}\text{O}_{64}]^{4+}(4e^-)$ ," *Advanced Materials*, Vol. 16, No. 8, 2004, pp. 685-689.
- <sup>7</sup>Toda, Y., Yanagi, H., Ikenaga, E., Kim, J. J., Kobata, M., Ueda, S., Kamiya, T., Hirano, M., Kobayashi, K., and Hosono, H., "Work Function of a Room-Temperature, Stable Electride  $[\text{Ca}_{24}\text{Al}_{28}\text{O}_{64}]^{4+}(4e^-)$ ," *Advanced Materials*, Vol. 19, No. 21, 2007, pp. 3564-3569.
- <sup>8</sup>Kim, S.W., Shimoyama, T., and Hosono, H., "Solvated Electrons in High-Temperature Melts and Glasses of Room-Temperature Stable Electride  $[\text{Ca}_{24}\text{Al}_{28}\text{O}_{64}]^{4+}(4e^-)$ ," *Science*, Vol. 333, No. 6038, 2011, pp. 71-74.
- <sup>9</sup>Toda, Y., Kubota, Y., Hirano, M., Hirayama, H., and Hosono, H., "Surface of Room-Temperature Stable Electride  $[\text{Ca}_{24}\text{Al}_{28}\text{O}_{64}]^{4+}(4e^-)$ : Preparation and Its Characterization by Atomic-Resolution Scanning Tunneling Microscopy" *ACS Nano*, Vol. 5, No. 3, 2011, pp. 1907-1914.
- <sup>10</sup>H. E. Gallagher, "Poisoning of LaB6 Cathodes," *Journal of Applied Physics*, Vol. 40, No. 13, 1969, pp. 44-51.
- <sup>11</sup>J.B. Scott, (1981) *Thermionic Emission and Space-Charge Theory*, Avionics Laboratory at Wright-Patterson Air Force Base, Ohio.
- <sup>12</sup>McDonald, M. S., Gallimore, A. D., and Goebel, D. M., "Note: Improved heater design for high-temperature hollow cathodes," *Review of Scientific Instruments*, Vol. 88, No. 2, 2017, pp. 026104.
- <sup>13</sup>Kim, S.W., Miyakawa, M., Hayashi, K., Sakai, T., Hirano, M., and Hosono, H., "Simple and Efficient Fabrication of Room Temperature Stable Electride: Melt-Solidification and Glass Ceramics," *J. Am. Chem. Soc.*, Vol. 127, 2005, pp. 1370-1371.
- <sup>14</sup>Trofymuk, O., Toda, Y., Hosono, H., and Navrotsky, A., "Energetics of Formation and Oxidation of Microporous Calcium Aluminates: A New Class of Electrides and Ionic Conductors," *Chem. Mater.*, Vol. 17, 2005, pp. 5574-5579.