Development of a C12A7 Electride Hollow Cathode

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Abstract: The current state of development of a hollow cathode featuring the unique emitter material C12A7 electride is described. C12A7 electride is a promising material with an extremely low work function down to about 0.6 eV, allowing low operational temperatures and low-voltage ignition at low temperatures. The electride material is developed jointly with the Fraunhofer IKTS in Dresden. One of the main challenges seems to be the overheating of the insert, therefore a thermally improved design was developed. With such a design, operation in the range of 2 A was stable for up to five minutes at the time, before the cathode seemed to overheat.

I.Introduction

WITH many different successful in-orbit operations in the last couple of years, electric propulsion systems became more and more interesting for the usage on spacecraft systems. To operate these thruster systems, highly efficient electron sources are needed: On the one hand for the neutralization of the ion bean to prevent the charge up of the spacecraft, and on the other hand for the general operation of some electrical thruster systems, like for example the gridded ion thruster[1] or the Hall-effect thruster[2]. For such an electron source, hollow cathodes established themselves amidst the electric propulsion systems.

Still, there could be several possibilities to improve the performance of state of the art hollow cathodes. One of these possibilities would be the usage of an improved low work function material as the emitter material. In recent years, a promising candidate for such a material has been found, namely the C12A7 electride, which could have a work function as low as 0.6 eV,[3] compared to the 1.5 eV[4] – 2.6 eV[5] for state of the art materials.

A hollow cathode featuring this unique material is currently developed at the advanced propulsion laboratory of the Institute of Aerospace Engineering at the Technical University of Dresden. Advantages of the material would for example be the much lower operation temperature of the cathode as well as the ignition of the cathode from room temperature.[6,7] Therefore, no heater would be needed any more, enabling a simplified and condensed design as well as reducing the risk of failure. Furthermore, with no heating needed anymore, the operation could be shortened enabling instant ignition of the cathode and therefore the thruster. Such a condensed design would be, among others, ideal for small satellite missions like CubeSat's.

This paper will give an overview of the unique material C12A7 electride and past results of the test with such a hollow cathode. We will then discuss our ideas to improve the performance of a C12A7 electride cathode, especially

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in order to get long time emission without degradation of the insert material. Based on these changes, we will be presenting first results of a new design and the operation of the cathode. Finally, we will be discussing the current state of the cathode as well as the further work that is planned.

II. The C12A7 Electride

C12A7 is an abbreviation for the calcium aluminate ceramic 12CaO · 7Al2O3. It is a substitute of different kind of cements and natural occurring in *Mayenit*. The ceramic itself does have a bandgap in the order of 7 eV and is therefore a great insulator.[8]

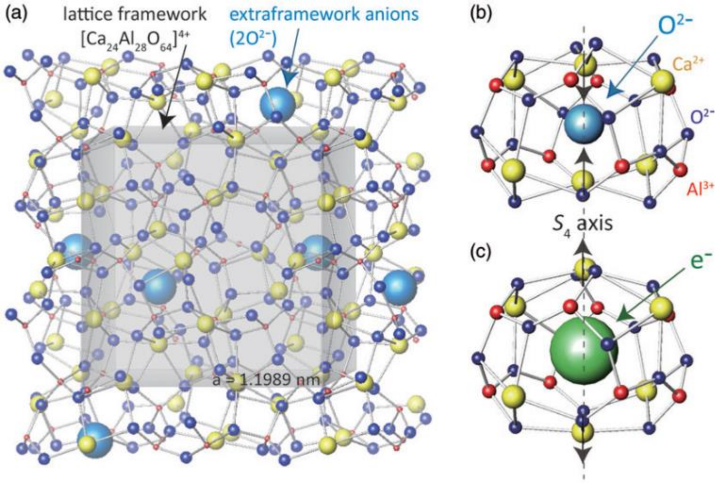

Figure 1. C12A7 unit Cell and nanocages. a) *Lattice framework of the ceramic with unit cell in the gray box, b) nanocages with oxygen anion inside, c) nanocages with electron inside*.[8]

The unit cell of the material is built of 12 nanocages, each about 0.4 nm in diameter. The framework itself is positively charged, and for neutrality of the unit cell, two oxygen (O^{2-}) ions are randomly distributed in those nanocages (Fig. 1).[3] Unique for the ceramic would be that these O^{2-} Ions can be exchanged with different kinds of anions like Cl^-, F^- or H^-, each creating a different set of properties for the material[9]. Ultimately, these two oxygen ions can also be exchanged by four electrons, creating a so-called electride. An electride is a material, in which electrons act as anions. The electrons are typically not bound to one molecule in particular, but rather free to move in the compound.[9]

Compared to other known electrides, the C12A7 electride is stable at room temperature as well as up to 900 °C.[10] Because the electrons are much smaller than the oxygen ions, they can move between the nanocages much more easily, which is called the cage hopping. The ceramic therefore becomes electrical conducting and exhibits a low work function, theoretically in the order of 0.6 eV.[3,9,11]

There are several different ways to fabricate the C12A7 electride, each giving significant information about the properties of the material. These processes were described in detail by Kim et al., who distinguished three distinct procedures.[8]

For the first option, there would be the production of the normal ceramic followed by a specific treatment, where the material would be heated in a reduced atmosphere. The oxygen ions would be pulled out of the material and exchanged by the electrons.[8] In the second option, the electride can be fabricated directly from the melt, when the solidification process is done in a reduced atmosphere.[8] Alternatively, the melt could also be cooled in a vacuum, improving the production time, as fewer steps are needed.[6] In the third option, the electride crystal could be grown directly, using for example the Czochralski process with well-defined (atmospheric) parameters.[8]

Whatever option is chosen, important for each of these procedures seemed to be the presence of some kind of template anions, which are needed as stabilizer to form the framework. Without these, the mixtures would decompose to other phases (C3A and CA). Different template ions do need different atmospheric compositions. For the fabrication of the electride form, typically carbon anions (C^{2-}) are needed as they allow the buildup of the framework and release the electrons during the solidification process.[8,9]

Looking at the different fabrication processes it is clear, that the material seems to be rather sensitive to different atmospheric conditions as well as material interactions, especially when heated. It therefore must be guaranteed during operation, that the electride would not decompose to some other eutectic, losing its unique properties. Furthermore, one has to be aware during the design of a cathode that the melting point is below the typical operation temperature of a hollow cathode. Next to the low melting point (1415),[3] there is also the low thermal conductivity (4.5 $Wm^{-1}K^{-1}$) to be considered.[12] At last, there seems to be a significant influence of the surface condition of the material, especially oxides and contaminations, possibly corrupting the low work function properties.[6,13]

III.Previous Work

The C12A7 electride as emitter material for hollow cathodes was first used by Rand et al. at the Colorado State University.[6] Rand fabricated the material herself in a vacuum furnace, and did cut parts of the material out of the carbon crucible. The insert lacked therefore a defined geometry. Nevertheless, the cathode could be started without any heater and operated for several hours.[6] Work function test did show low values in the order of 0.76 eV but did worsen with time. In the end, the cathode was also tested with iodine as alternative propellant, with promising results as no degradation could be observed.[6]

Drobny et al did first tests of a hollow cathode with defined insert geometry[7]. The insert was shaped as hollow tube with an inner diameter of 1.2 mm, 3.5 mm outer diameter and 8.4 mm length. The cathode was ignited without any heater, but only operated for some seconds at the time, before it went out. The stability of the plasma could be increased with higher emission currents, which at the same time lead to an increased heating of the cathode. Because of this heating, the temperature rose above a critical temperature as the insert as well as the barrel material (stainless steel) did melt.

Even though the insert material was in a rough shape already, the cathode was tested successfully with a Hall-effect thruster with an emission current in the order of 4 A total. The ignition was instant and could be repeated several times. Because of the fast increase in the temperature, emission was stable for only about 10 to 20 seconds, before the cathode typically started to glow and was shut down / went out. A typical appearance of the thruster and a characteristic of voltage and current can be seen in Fig. 2.

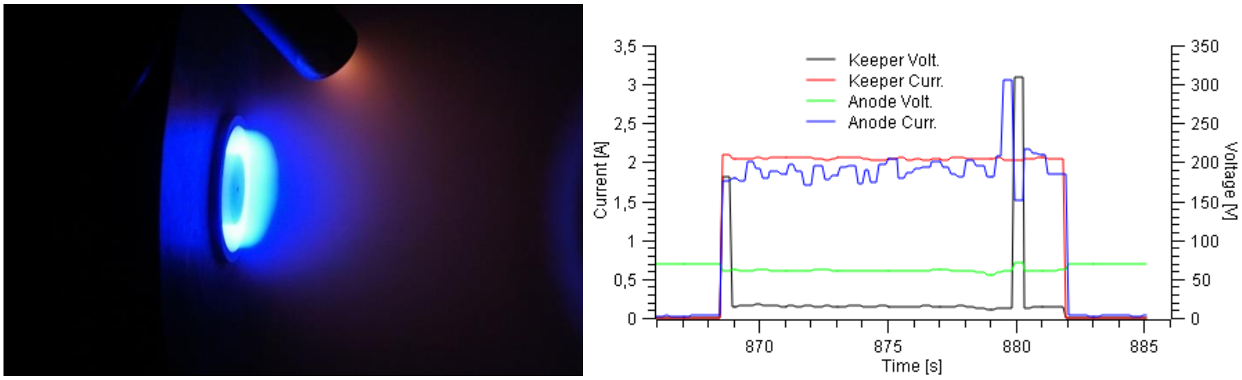

Figure 2. Hall-effect thruster operation with C12A7 Cathode. *Optical appearance of the Hall-effect thruster with corresponding voltage and current characteristic. Operation was stable for 15 seconds before being shut down. The current limits at keeper and anode were set at 2 A each*[7].

IV. Improving the performance of the cathode

While analyzing the previous tests it was apparent, that the temperature at the insert got too high. During the operation of the cathode, the tip of the keeper cathode started to glow, indicating a temperature in the order of at least 600 °C. Assuming that the vast majority of the generated heat is induced in the cathode (cathode orifice) and from there radiated outwards to the keeper, the temperature at the insert will be much higher. Furthermore, melted pearls appeared during operation in the keeper orifice and the surface of the insert did look like it was melted and solidified rather than being crystalline.

Direct temperature measurements close to the cathode orifice could not be done, only at the backside of the cathode base. Nevertheless, temperatures above 200 °C have been measured, supporting the theory of too high of a Temperature at the tip of the cathode. Apparently, the heating of the insert does not regulate itself in a way expected from the hollow cathode. Therefore, the thermal balance of the entire system should be adapted accordingly. The usage of stainless steel as cathode barrel material seem to be unsuitable, as the heat is accumulated at the tip of the cathode, where the insert will melt. Furthermore, the thermal resistance of stainless steel is too low, especially for the orifice geometry, as high thermal heating occurs, even though low operation temperatures are theorized. This leads to the destruction of the cathode barrel material.

Based on the observations and the experience gained, a new design of the construction of the cathode has been done, which can be seen in Fig. 3. The main focus was on the thermal balance of the system, which was tested with a simple thermal model. The idea was to conduct the heat away from the insert, in order to prevent the melting.

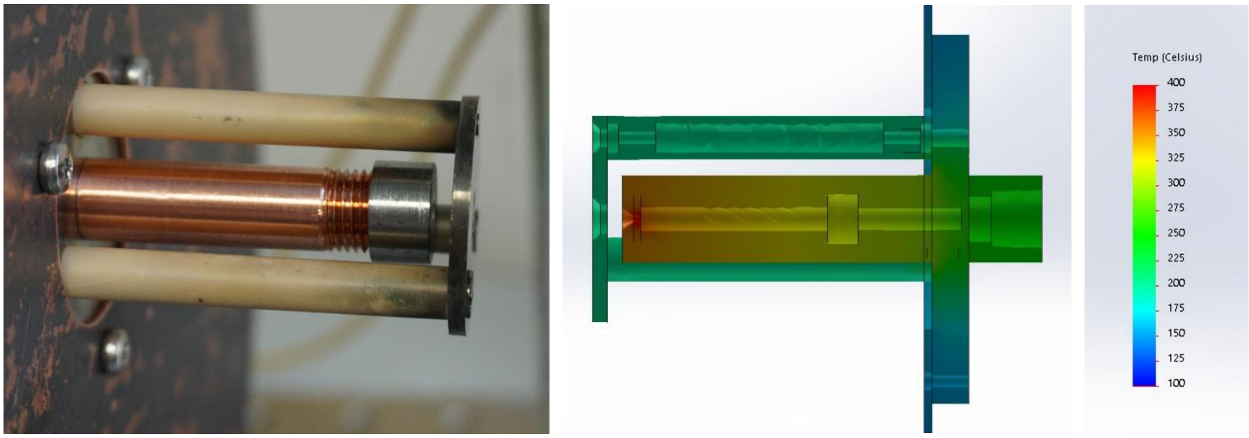

Figure 3. New Design of the cathode with simple thermal model. *Cathode barrel made of copper with molybdenum orifice screwed on top. The keeper is hold and isolated with the aluminum oxide tubes. Cathode barrel and aluminum oxide tubes are mounted on the cathode base, where also the radiator as well as the electrical connections are attached. Corresponding to the design the temperature distribution simulated with a thermal model with a heating power of 40 W at the cathode orifice.*

The cathode barrel is now made of copper, which features a much higher thermal conductivity as well as capacity than stainless steel. Different other materials were tested, as can be seen in Fig. 3, but got ruled out because a too high temperature (stainless steel) or a too low melting point (aluminum). At the same time did the wall thickness increase significantly to have a greater cross section available for thermal conduction. At the backside of the cathode, a radiator was installed. The radiator was made of oxidized copper in order to have a high emissivity and homogeneous temperature distribution to radiate enough heat from the else isolated cathode away. Because of his form, the radiator was also used as plasma shield, so secure the electrical connections at the backside of the cathode.

The cathode orifice is made of molybdenum, being much more temperature resistant than the stainless steel. The orifice will be screwed on top of the cathode barrel. There have been several different geometries for the orifice, ranging from type “A” (small orifice with great length-to-diameter ratio) to type “C” (no orifice) cathodes[14,15], in order to evaluate the most suited geometry for starting and operation. The Keeper was made in a somewhat open configuration, meaning that the Keeper front plate was only held by three Al_2O_3 tubes. This allowed the observation of the cathode orifice directly from outside of the chamber.

Another Challenge using the C12A7 electride that seemed to be apparent was the conduction of the insert to the cathode barrel. Thermally, as the rough surface and brittleness of the insert prevented a tight fit of the cathode barrel, and electrically, as oxide layer could possible increase the resistance between the insert and the barrel significantly. Therefore, a gold coating of the insert was tested (Fig. 4). The inserts available were coated at the front face or the lateral surface, as well not at all as reference. Furthermore, there was some kind of conduction paste available, to conduct the insert to the cathode tube. The paste was a compound of silver and palladium, and could easily applied to the insert.

Figure 4. Gold coating on the surface of the insert. *Three different kinds of gold-coated inserts have been available for testing. a) The gold is coated at the lateral surface of the insert tube, b) the gold is coated at the front side of the insert tube, c) reference insert with no gold coating at all*

V. Test Setup

The test campaigns of the C12A7 electride hollow cathode were done in the advanced propulsion laboratory at the Technical University of Dresden. For the tests, a vacuum chamber with 500 mm in diameter and 1 m length was available. On top of the chamber is a cryogenic pump installed (nominal airflow 10,000 l/s), with which a base pressure without gas ballast in the order of 1E-7 mbar is reached. With gas ballast during operation, the pressure will normally be in the range of 1E-4 mbar.

For the electrical operation of the cathode, two *Delta Electronica SM660-AR-11* power supplies were used. The power supplies each have a maximum voltage of 660V and maximum current of 11A, at a maximum power output of 3.3 kW. To verify the currents flowing, the current to the "ground"-potential of the cathode was measured at a pre-resistor (current calculated using the voltage drop over the resistor measured with *LabJack*).

The cathode was operated with argon, which was controlled by mass flow controllers from *Brooks Instruments*, model family GF40. Using this calibrated system, a calibration error of the previously used needle valves got obvious, having resulted in mass flow rates about 20 times lower than they actually were.

The cathode was assembled outside of the chamber on top of an aluminum breadboard (Fig. 5). The cathode was only connected to the gas feed, which itself was mounted on an isolator, therefore isolating the entire cathode system from the chamber potential and allowing the biasing of the cathode potential and the measurement of the current flowing into the cathode. As anode, a copper tube with 100 mm in diameter was positioned about 100 mm in front of the cathode.

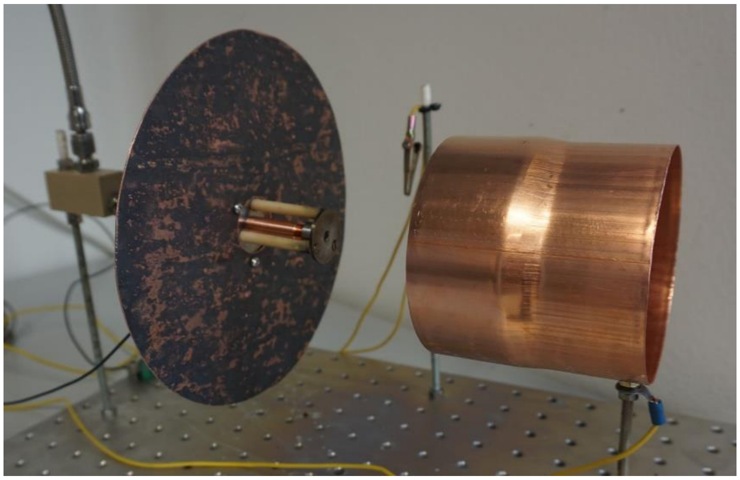

Figure 5. Test setup. *The hollow cathode as well as the anode and filament mounted on the breadboard for operation in the vacuum chamber.*

VI.First results

The new design was tested in the vacuum chamber described in the previous section, starting with small orifice diameters for a type "A" cathode, to minimize the mass flow rate. In the beginning of the tests, there were significant problems with the ignition of the cathode. Higher voltages as well as higher mass flow rates were tested, without sufficient success. Apparently, the small orifice diameters are not suited for the heater less ignition, as the electric field probably does not penetrate the cathode enough. Therefore, a much bigger orifice in the order of the inner diameter of the insert was tested (type "C" cathode).

With such a type "C" cathode ignition did occur, but unreliable. Even though some plasma sparks did appear, no stable emission was reached. This could be changed with the implementation of an additional filament outside of the cathode. The filament was positioned about 15 cm away from the cathode and heated to about 2000 °C (bright yellow glow). To further improve the ignition behavior, the cathode was started at higher currents (4 – 5 A) as it was supposed to be operating (1.0 - 1.5 A). With higher currents the ignition and operation of the cathode was stable, but only for some seconds before it went out.

To increase the time of operation of the cathode, the current limits were decreased after ignition. With such a procedure, longer operation times could be achieved. A current and voltage characteristic of one of such test can be seen in Fig. 6, where emission was stable for about 75 seconds before being shut down. The diagram shows the decrease of the current limits, from 1.0 A at the keeper and 5.0 A at the anode to 0.5 A and 1.0 A respectively. The voltage during operation ranged around 35 V to 40 V at the keeper and around 65 V at the anode. The filament was shut down after some seconds of operation. The mass flow rate through the cathode was constant at 20 sccm, but there was an additional mass flow needed (about 10 to 100 sccm), to increase the pressure in the chamber.

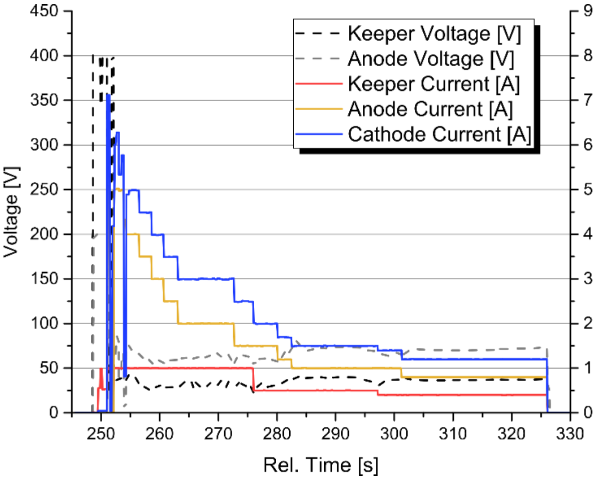

Figure 6. 75 s operation of insert. *Stable emission at 0.4 A keeper current and 0.8 A anode current.*

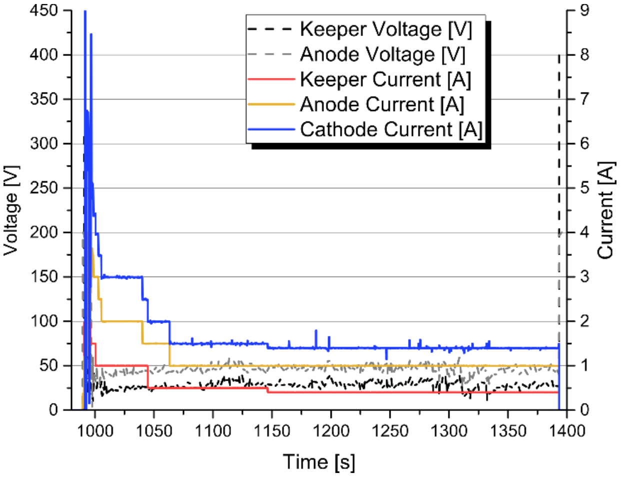

Figure 7. 300 s operation of insert. *Stable emission at 0.4 A keeper current and 1.0 A anode current.*

Typically, several of such ignitions did occur in one test campaign. Figure 8 shows the front side of the insert inside after several test campaigns. On the outside of the insert, there is still the crystalline structure on the surface, but on the inside, there seemed to be a melted and solidified phase. Such observations point towards a great increase in temperature at least at the surface of the emitter material. The backside of the insert typically did not show any sign of increased temperature, pointing towards the low thermal conductivity of the material. Nevertheless, the high temperature at the front side must be avoided.

In order to find more suitable operation points of the cathode, we also experimented with higher mass flow rates through the cathode. At around 80 sccm, ignition occurred without having any other mass flow into the chamber. At such a high mass flow rate, the longest operation of the cathode could be achieved. The corresponding characteristic can be seen in Fig. 7.

As discussed before, the cathode was started with a filament and at high emission currents, which were dialed down after a stable plasma condition was achieved. In this case, the current at the keeper was set to 0.4 A and 1.0 A at the anode. Voltages ranged at the keeper between 15 V and 35 V and at the anode between 35 V and 55 V. The mass flow rate was set at 100 sccm. It is believed, that this rate could have been dialed down, but because of the stable emission, no changes were done to the general operation of the cathode. The cathode emitted for about 300 seconds, before it went out.

During operation of the cathode, in general as well as during the test explained previously, several different plasma conditions were observed. An overview of the appearance from some notable conditions is given in Fig. 9. In Fig. 9 a), there is a clear blue plasma cone right at the keeper orifice, which is indicative of desirable hollow cathode operation. Unfortunately, this was not always the case. To give an example of the different kinds of plasmas, Fig. 9 b) to 9 d) show the appearance during the longest test done with the cathode (about five minutes), as it was earlier described and as plotted in Fig. 7.

Figure 9b) shows a wide white plasma cone towards the anode, which is rather diffuse. Figure 9 c) shows an intense and bright yellowish glow between the cathode orifice and the keeper orifice. In front of the keeper, there is short diffuse plume with more of a red color. Figure 9 d) is again of a more whitish color, but this time the plasma does not reach up to the anode but rather seems to be a ball, which floats right in front of the keeper, but separated from it.

Even though there has nearly been no change in the parameters for the operation of the cathode, the changes in the plasma seem to be significant. Unfortunately, no clear conclusions can be drawn from the plasma appearances but these images capture the inconsistencies observed in the plume even when the operating parameters remained relatively unchanged. In future work the goal will be to get consistent performance within and outside the cathode.

Figure 8. Degradation of insert. *The insert melted at the tip after several ignition attempts.*

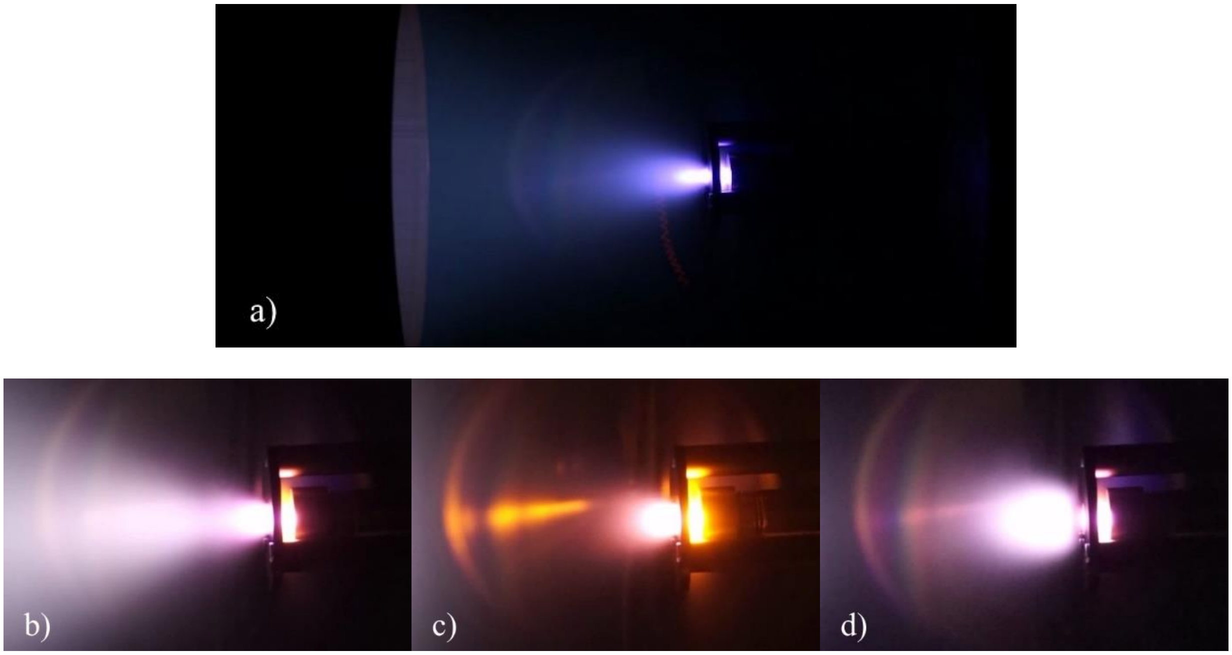

Figure 9. Hollow cathode plasmas during operation. *Different appearances of the plasma at the cathode during stable emissions. Changes in color, shape and intensity. a) Clear blue plasma cone, b) diffuse white plasma, c) orange to red plasma, d) white plasma disconnected from the keeper.*

VII. Conclusion

This effort is the first step in our development of a C12A7 hollow cathode. Overall, our improvements to the thermal design considerably improved the overall behavior of the cathode but still resulted in inconsistent performance and behavior in the plume. Although the thermal conductivity of the cathode barrel was increased significantly, the insert still melted at the front surface. These results show that further improvements to the electride insert material and the overall cathode are still needed. Next steps will concentrate on an improvement of the material itself and its characterization as well as changes in geometry and further long-term testing.

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