LaB$_6$ hollow cathode work function enhancement: insight into the chemical processes.

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LaB$_6$ hollow cathodes have demonstrated robust performance as electron emitters for electric propulsion applications throughout the years. In our recent work,$^1$ we discovered that cathodes based on this material exhibit a transient thermal behaviour during the first 50 h of operation that we attributed to the response of a reduction of the net work function of the cathode emitter. In this work we establish the possible chemical reasons for such improvements and study some of them with chemical analysis. The hypotheses for the reduction include crystallographic evolution of the polycrystalline sample, phase change of the emitting surface, forced lanthanum termination of naturally occurring boron-terminated crystals and chemical poisoning of the surface. In order to investigate these hypotheses, we designed and built a modified insert which contains a small portion of flat emitting surface exposed to the collisional plasma in the cathode interior. This small piece was built to be removable and therefore, we could extract it from the cathode and place it inside an ultraviolet photoelectron spectrometer (UPS) for work function measurements, electron backscatter and an X-ray diffractometer for crystallographic measurements, secondary electron microscope for morphology identification, and a profilometer for topology characterization. The results from these analyses allowed to characterize the morphological and chemical modification resulting from the action of the plasma on the emitting surfaces of a LaB$_6$ cathode running at 25 amps and 13 sccm. They also aided in isolating the mechanism behind the lowering of the work function. Work function measurements with UPS confirmed that the work function is reduced permanently after plasma exposure. However, there may also be secondary factors that further reduce the work function temporarily during operation, such as forced La termination. No phase change was observed at the surface of the sample after cool down.

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Finally, we observed a crystallographic texture formed by the action of the ions impacting on the walls of the cathode emitter, which can explain the work function reduction. The work function reduction due to the action of the cathode plasma is a recently found phenomenon\(^1\) which greatly benefits the lifetime of polycrystalline LaB\(_6\) hollow cathodes. As a result of identifying the mechanism behind the reduction, we can now pre-process the inserts that will be used in space cathodes to yield the best possible lifetime. Similarly, we can design the geometry of the cathode to make sure the beneficial crystallography is exposed throughout the lifetime of the cathode.

**Nomenclature**

- MPD = magnetoplasmadynamic
- DFT = density functional theory
- SEM = scanning electron microscope
- XRD = X-ray powder diffraction
- EBSD = electron back scatter diffraction
- HIP = hot isostatic pressing

**I. Introduction**

Electric propulsion plays a crucial role in space exploration. From satellite station keeping to deep space travelling, Ion Thrusters and Hall effect thrusters have proven to be very useful tools to accomplish the end goal of reaching further into the unknown. Furthermore, emerging variants of more classical designs like the MPD thruster promise increasing even more the application range of EP devices. Hollow cathodes are essential components for the performance of any of these thrusters. So much so, that if the cathode fails prematurely, the whole thruster is rendered unusable.

Unfortunately, cathodes are complex devices which require a multiphysics approach to fully understand them. At the heart of the behavior of hollow cathodes is the cathode plasma which provides a conductive medium that connects the electron emission source to the thruster plasma or ion beam. The electron emitter provides the electrons necessary to sustain the cathode plasma and therefore the thruster operation. The materials used as electron emitters must exhibit several characteristics; low work function, low evaporation rate and high poisoning robustness to propellant impurities, among others. Several materials have been selected and tested throughout the years to be used as emitters. Two technologies are widely used today in electric thrusters, namely: BaO-W and LaB\(_6\).\(^2\)

LaB\(_6\) hollow cathodes have proven to be a very robust technology after many years of use in operating spacecraft. However, the specifics of their operational behavior are still evading our understanding. In our previous work,\(^1\) we found that the cathode behaves as if it had a work function lower than the classically accepted value for LaB\(_6\) vacuum cathodes, 2.67 eV.\(^3\) In order to estimate precisely the work function of LaB\(_6\) in the hollow cathode configuration, we built a coupled 2D axisymmetric plasma and thermal model.\(^4\) Based on the final result for the coupled system we estimate a work function of 2.25 eV for the cathode with a 25 A discharge and 13 sccm mass flow rate of xenon. This is 0.42 eV lower than the vacuum cathode value.

The specific mechanism responsible for the reduction in work function is of great importance, not only from a purely scientific point of view, but also from an engineering one. Once the mechanism for the reduction is identified, we can potentially use it to engineer LaB\(_6\) hollow cathodes for even lower operating temperatures throughout the lifespan of the cathode. With this new design, we could maximize the lifetime of polycrystalline LaB\(_6\) cathodes.

The work function of a crystalline solid is a surface property of its crystals. It is an energy barrier established by the local environment of the crystal atomic structure at the surface. Therefore, it can be affected by numerous mechanisms. It is challenging to isolate a singular mechanism that can impact the work function in a given direction, because work function is determined by fine details of the atomic structure at the material surface. We have used published results from density functional theory\(^5,6\) (DFT) to elaborate the hypothetical mechanisms behind the work function reduction in LaB\(_6\) presented in this work. We have identified four possible mechanisms that could improve the work function of polycrystalline LaB\(_6\):

1. Formation of a crystallographic texture promoted by the preferential removal of high surface energy
crystals due to the actions of the ion return current to the emitting surface of the cathode.

2. Formation of LaB$_4$ due to the re-crystallization of LaB$_6$ in a La-rich environment.

3. Formation of a cationic termination in otherwise naturally occurring Boron terminated crystals.

4. Formation of a surface complex upon the interaction of LaB$_6$ with a chemical specie outgassed from a component in the vicinity of the emitter.

The polycrystalline LaB$_6$ inserts used in our studies are manufactured from LaB$_6$ powder synthesized using carbothermal reduction$^7$ and subsequently milled into 2µm mean grain size. The powder was manufactured by Treibacher Industrie AG. The powder was then sintered into a billet by means of hot isostatic pressing in a Ta crucible by Exothermics Inc. Subsequently, the billet is machined into the final shape of the emitter using electro-discharge-machining (EDM). Throughout the synthesis of the powder, consolidation into the billet, and machining into the final emitter shape, there is no mechanism that preferentially exposes any one type of LaB$_6$ crystal at the surface. Thus, the exposed crystallographic orientation at the surface of the emitter does not show any specific crystallographic texture; it is completely random. That is the state of the emitting surface when the work function of polycrystalline LaB$_6$ samples is measured by means of a Richardson plot in a vacuum diode test cell.

In this work, we have studied the effect of the hollow cathode plasma interacting with the emitting surface of a polycrystalline LaB$_6$ insert. To that end we have built a slightly modified version of the classical cylindrical shaped insert, with the objective of exposing a flat surface of LaB$_6$ to the plasma. We then operated the cathode uninterruptedly for 50 hr at 25 A and 13 sccm. We have characterised the effect of the plasma on the surface by means of crystallographic, chemical and morphological analyses. Upon comparison of the data obtained with the control measurements taken in the unexposed sample, we were able to determine that formation of a crystallographic texture likely contributes to the work function reduction.

II. Methods

The objective of this work is to elucidate, from a chemical point of view, what causes the work function reduction in the LaB$_6$ hollow cathode configuration. We have focused our attention on the case where the cathode is operating at 25 A and 13 sccm. From our previous experience at this operating condition, we know that the cathode exhibits a transient behavior during the first 50 hr of operation and at that point, the thermal response of the cathode is very stable. Thus, we replicated that experiment but this time we used a modified insert that could help us understand the chemical evolution that occurs during the transients.

We prepared an experiment that consisted of exposing a polycrystalline LaB$_6$ sample for the first time since manufacturing to Xe plasma in the cathode over a period of 50 hr. The shut down sequence was designed to minimize any further evolution of the thermionic surface due to the cool down transient of the cathode. We designed a special vacuum chamber to cool down the cathode as quickly as possible after the experiment to reduce further chemical evolution of the thermionic surface due to high temperature (diffusion of chemicals at the surface or recrystallization). The chamber is described in section A. We obtained very steep cool down rates (starting at 246 °C/min) and total cool down of the insert in 5 hr. Additionally, we kept the Xe flow running until the insert temperature reached room temperature to prevent any chemicals from the vacuum chamber from reaching the sensitive thermionic emitter surface while it cools down from operating temperature (> 1200 °C).

A. Test article and facility – insert, cathode and chamber

The cathode setup used in this experiment was described in.$^{1,4}$ The only difference with that configuration is the use of a modified insert geometry in this study. The modified insert is shown in Fig. 1.

The insert consists of two pieces, part A and part B. Part A is held in place by its own weight in part B. Part A can be easily placed inside part B as in Fig. 1 and it can also be easily removed and transported for chemical analysis. This new geometry has an available area for thermionic electron emission 1.72% smaller than the original insert.

The chamber in which this experiment ran has a volume of $22 \times 10^{-3}$ m$^3$ and two 10$^7$ cryopumps arranged in opposite directions to each other (Fig. 11), the cathode sits between them (Fig. 2).
B. Operating conditions

The cathode operating point chosen for the 50 hr test had been studied previously and results were shown in.\textsuperscript{1,4} The discharge was set at 25 A and the mass flow rate at 13 sccm.

C. Surface morphology characterization – scanning electron microscopy (SEM) and profilometry

In order to visualize the effect of the plasma on the sample of LaB\textsubscript{6}, a series of high resolution images were obtained using a scanning electron microscope, ZEISS 1550VP FESEM. This device is located at the Caltech GPS Division Analytical Facility. The objective was to characterize the surface before and after plasma exposure. In SEM, accelerated electrons are forced to collide against a surface. When the electrons interact with the sample, they are decelerated by inelastic collisions, producing a variety of signals. One of these signals is the secondary electron emission, which is used to produce SEM images. Backscattered electrons are also emitted and they are mostly used for illustrating contrasts in composition in multiphase samples.

To quantify the effect that the plasma had on the morphology of the surface exposed to the plasma of part A (highlighted surface in Fig. 1), we used a DektakXT stylus profilometer. This device is located at the Caltech Molecular Materials Research Center. Stylus profilometers measure the surface profile of a sample by physically moving the tip of a probe along the sample surface. The method consists of applying a constant force to the stylus and maintaining it through a feedback loop. The change in the height of the arm holder is then measured and the profile can be reconstructed from the data. The radius of the stylus is 2\textmu m, profile configuration was \textit{“Hills and Valleys”} and the stylus force was 3 mg. We selected the best possible resolution depending on the surface roughness present in the sample, which was either 6.5\textmu m or 65.5\textmu m peak to peak. Profiles along five straight lines were obtained before and after the plasma exposure. Those lines are shown in Fig. 3. Note that the profile could not be extended to the edges of the sample due to limitations in the apparatus.

D. Direct work function measurement – ultraviolet photoelectron spectroscopy

The work function was measured directly in the test sample after plasma exposure along Line 3 (see Fig. 3) in 15 different locations by ultraviolet photoelectron spectroscopy (UPS) using a Kratos Ultra spectrometer.
In UPS, the work function can be spectroscopically acquired by measuring the difference between the Fermi level and the cutoff of the tail at the low kinetic energy end of the photoemitted electrons of the sample, and subtracting this value from the incident photon energy (see Fig. 12). After the 50 hr test finished, the sample was exposed to the atmosphere in order to be transported from the vacuum chamber where the cathode was run (Jet Propulsion Laboratory), to the UPS instrument located at Caltech. The work function was also measured at five randomly chosen locations in a control sample. The control sample belongs to the same billet from which the insert was extracted. The surface of the control sample where the work function was measured was produced by cracking a control piece of LaB$_6$ with a pair of pliers right before introducing it into the UPS. The exposure of that sample to the atmosphere was less than 10 min. To account for possible area effect on the work function measurement, we used five different focusing lenses in the UPS instrument. According to the manufacturer of the apparatus, the different settings correspond to the following approximate areas: $1 \times 1 \, \text{mm}^2$, $110 \times 110 \, \mu\text{m}^2$, $55 \times 55 \, \mu\text{m}^2$, $27 \times 27 \, \mu\text{m}^2$ and $15 \times 15 \, \mu\text{m}^2$. We checked the calibration of this technique by measuring the work function of a sputtered polycrystalline gold sample at one location, using each of the aforementioned apertures, and obtained values which deviates from the nominal value of 5.1 eV by less than 0.014 eV, a mean 5.086 eV with a standard deviation 0.037 eV.

E. Phase identification – X-ray powder diffraction and electron backscatter diffraction

X-ray powder diffraction (XRD) and electron backscatter diffraction (EBSD) are techniques useful for the characterization of the different phases present in a sample. Both of these techniques require flat samples to obtain meaningful results, which drove us to the design shown in Fig. 1.

EBSD is a surface analysis technique that allows quantitative microstructural analysis in SEM up to a nanometer scale. In this method, a beam of electrons is focused at the point of interest on a tilted sample, typically at $70^\circ$ from the normal to the surface. Upon inelastic interaction between the impinging electrons and the atomic structure of the sample surface, scattered electrons form a divergent source of electrons close to the surface of the sample. Some of those electrons interact with the structure at angles that satisfy the Bragg equation: $n\lambda = 2d\sin(\theta)$ where $n$ is an integer, $\lambda$ is the wavelength of the electrons, $d$ is the spacing of the diffracting plane, and $\theta$ the angle of incidence of the electrons on the diffracting plane. The diffracted pattern is recorded on a phosphor screen where the so-called Kikuchi bands are recorded. Each Kikuchi band can be indexed by the Miller indices of the diffracting crystal plane which formed it, thus enabling crystallographic identification. By comparing the measured Kikuchi patterns with known patterns from a database, phase identification can be obtained. Penetration depth in the order of 10 nm is characteristic for this technique, albeit dependent on the material. We applied this technique at locations of interest in the test sample after it was used in the 50 hr run test. The area analyzed in each case was 1 mm$^2$. The speed of acquisition was 40.53 Hz and the accelerating voltage was 20 kV. The EBSD system used was manufactured by KHL Technology and is located at the Caltech GPS Division Analytical Facility.

XRD is another surface analysis method that provides information about the crystalline nature of materials at penetration depth of around 10 $\mu$m. Similarly to EBSD, XRD employs constructive interactions between X-rays and atomic structures, producing patterns that can be recorded and used against database information to deconvolve the different phases present in the sample. The directions of possible diffractions depend on the size and shape of the unit cell of the material. The relative intensities of the diffracted X-rays depend on the kind and arrangement of atoms in the crystal structure. In order to produce a unique pattern from a crystalline material, the atomic structure needs to be exposed to the incident X-ray beam in every possible direction. This is obtained in practice by producing a powdered sample from the crystalline material of
interest. The powdered sample is typically called a polycrystalline aggregate or powdered material. When a powder with randomly oriented crystallites is placed in an X-ray beam, the beam will expose all possible interatomic planes. If the experimental angle is systematically changed, all possible diffraction peaks from the powder will be detected by the scintillation detector. By comparing the measured peak and intensity patterns with known patterns from a database, phases can be identified. We utilized a PANalytical X’pert³ XRD with Bragg-Brentano geometry operated by Professor K. Faber’s group at Caltech. The data was acquired at 0.31 °/min.

F. Crystallographic texturing – X-ray powder diffraction

X-ray diffraction as a technique is similar to measuring the diffraction from a single crystal that is rotated in every possible direction with respect to a fixed incident X-ray source. From that point of view, the XRD pattern represents the result of a perfectly random distribution of crystal orientations in the powder sample or similarly in the polycrystalline solid sample (our test article). This situation is described by saying that there is no crystallographic texture in the polycrystalline solid sample. As a consequence of this, if a texture is present in the sample, the relative intensities of the XRD peaks will change.

III. Results

A. Cathode operating conditions

The cathode was operated for 50 hr in the aforementioned vacuum chamber and its performance was measured with the data acquisition system introduced.¹ Fig. 4 shows the temperature of the insert measured with a Type C thermocouple for the 50 hr test. Fig. 13 shows the shut down procedure and cool down curve. Fig. 14 shows the main discharge voltage, current and keeper voltage during the test. Fig. 15 shows the vacuum chamber pressure and Xe mass flow rate fed into the cathode.

In Fig. 4 we can observe a temperature transient somewhat similar to the one introduced in.¹ The behavior of the transient is similar in terms of showing a fast cool down during the first 5 hr of the cathode operation and slower cool down during the following 45 hr. Of note, while the transients were highly reproducible, at this time we observed a temperature at steady state about 200 °C higher. Once we dissembled the cathode, we found that most of the thermionic active area of the insert part B was coated in black, see Fig. 16. The source of this contamination is most likely the graphite pusher placed upstream of the insert. Prior to this 50 hr test, the cathode assembly (including the pusher but excluding the insert) was thoroughly outgassed. The outgassing lasted for ~24 hr at 1300 °C. It is unclear whether the outgassing procedure was insufficient (higher temperature or longer processing time required) or this contaminant is sputtered off the pusher walls by energetic ions. Insert temperature increments due to carbon contamination have already been observed, see.¹ We believe that this contamination is the reason for the abnormal temperature at steady state in this test. Fortunately, the carbon contamination did not affect the test article (part A) significantly. Nonetheless, these observations highlight an important unsolved problem with LaB₆ cathodes, namely material compatibility. Given the knowledge available in the literature and from practitioners in the field, graphite is considered the best suited material to be in contact with LaB₆ at high temperature. This is also true given our own experience. However, in light of the contamination issues introduced here, more work needs to be done to perfect its utilization.

B. Morphology identification – scanning electron microscopy (SEM)

In Fig. 5 the microscopic evolution of the morphology of the surface of the material can be observed. The image on the left corresponds to a surface that was produced by electrical discharge machining (EDM) from the billet as the test sample. On the right we can observe the test sample after exposure to the cathode plasma for 50 hr. The most remarkable detail in the pictures is the faceted appearance of the surface that corresponds to the area of the test sample exposed to the high density plasma (downstream side or right hand side in Fig. 5). On the left hand side of the test sample (exposed to a much lower plasma density), the surface morphology seems to be increasing in roughness but facets are not visible.

C. Topology characterization – profilometry
The profiles measured along the five lines depicted in Fig. 3 before plasma exposure are shown in Fig. 17 and for the sample after plasma exposure in Fig. 18.

As can be observed, the sample roughness after EDM is on the order of 2µm peak-to-peak and deviation from flatness is on the order of 1µm. The spikes in Fig. 17 are small imperfections in the surface.

In Fig. 18 the profiles after plasma exposure show a roughness on the order of 2µm peak-to-peak in the upstream region of the sample ($\bar{z} \sim 0.1$) that increases up to 8µm peak-to-peak in the downstream region. Furthermore, we can observe the profiles deviating from the upstream flat region which correspond to the mass of insert lost due to the action of the downstream high density plasma. These results are in agreement with the morphology observed qualitatively in Fig. 5.

D. Direct Work function measurement – ultraviolet photoelectron spectroscopy

Results for the work function measurements are shown in Fig. 6. There are five color bands that correspond to the work function measurement obtained in the control sample in five randomly chosen locations. At every location, the work function measurements were acquired five times with increasing aperture size of the UPS.

E. X-ray powder diffraction results

XRD spectra before and after plasma exposure are shown in Figs. 19 and 20. In Fig. 19 it is obvious that the XRD profiles before and after the test sample was exposed to the cathode plasma are not aligned with
the lines that represent the peak locations for LaB₄. On the other hand, the match is significant when we compare the profiles with the peak locations for LaB₆, see Fig. 20.

F. Electron backscatter diffraction results

The results from the EBSD analysis can be found in Fig. 7. The phase identification map on the left corresponds to a 1 mm² area in the upstream end of the test sample, whereas the one on the right corresponds to the downstream end. As can be seen, the Kikuchi patterns belong to crystalline LaB₆. The patterns were also compared with La oxide, B oxide and LaB₄. Similarly to the XRD results, EBSD did not detect the presence of crystalline LaB₄.

IV. Discussion

Work function measurement by UPS

UPS was employed to directly measure the differences in work function at plasma-exposed and control areas of LaB₆ inserts by UPS (Fig. 6). First, it is important to note that all the measurements are above 3.3 eV, which is considerably higher than the value of 2.66 eV for polycrystalline LaB₆ obtained by Lafferty. These differences are not unexpected given that in the work of Lafferty, work function was estimated using a LaB₆ sample in a vacuum cathode configuration at high temperature and results were extrapolated using the Richardson plot method. In contrast, we measured the photoemission work function by UPS of a LaB₆ sample at room temperature that has been exposed to the atmosphere. We propose that the observed differences in the absolute values of the work function measurements are likely due to adventitious carbon or oxidation of the surface from exposure to air after the experiment was concluded. Despite these differences, since putative
atmospheric contaminants such as carbon are constant throughout the samples, the relative differences in work function measurements across the insert are still comparable.

The measurements for the control sample provided work functions ranging from 3.75 to almost 4.2 eV. However, in the case of the test sample, the work function measured at 15 locations along the emitter sample ranges from 3.3 to 3.86 eV. We believe this is a real trend in the work function of the sample, associated with exposure to Xe plasma. Consistent with this hypothesis, we note that the lowest values of the work function are found in the downstream region of the insert, about \( \bar{z} = 0.8 - 0.9 \). This is the region which was exposed to high density plasma and showed a faceted morphology, as can be seen in Fig. 5. It is reasonable to believe that the facets shown in Fig. 5 could correspond to the \( \text{LaB}_6 \) crystals which exhibit lower work function. Hence, the work function observed in the downstream end of the insert shown in Fig. 6 would be the effect of such texturing.

For each location, 5 apertures were used. The work function spread for each location can reach 0.15 eV in some of the measurements, and as small as 0.02 eV in other instances. It is unclear at this point the nature of this variability. In the sputtered gold sample, the range was 0.094 eV.

**Crystallographic analysis by XRD**

XRD showed that \( \text{LaB}_4 \) is not present in the crystalline form in the cathode sample before or after plasma exposure. However, it is possible that \( \text{LaB}_4 \) could be present in an amorphous state after the cathode cools. Nonetheless, amorphous substances are not facetted, as they lack lattice ordering. Given the facetted appearance of the downstream end of the insert surface in Fig. 5, we do not think that it is possible to find amorphous \( \text{LaB}_4 \) in this end of the cathode. Another possibility is that \( \text{LaB}_4 \) could be present while the cathode is running but it transitions to \( \text{LaB}_6 \) as the cathode cools down. The only locations where this might exist are in the crevices between the peaks shown in Fig. 5 and the upstream end of the insert. Fig. 8 shows a SEM picture of the surface, where crevices are easily distinguishable and hold an apparently amorphous substance. One possibility that explains the formation of amorphous substance in the crevices is quenching of melted material due to the fast cool down rates obtained at cathode shut down. The melting point of \( \text{LaB}_6 \) and \( \text{LaB}_4 \) are both above the cathode operating temperature, therefore, we do not believe this is the mechanism behind their formation. An alternative explanation is that the amorphous-looking structure in the crevices is not a sign of lack of crystallinity but is instead a result of ion etching. Crystals with high surface energy are more rapidly etched away than crystals with low surface energy (highly stable). The material in the valleys has lower chances of being impacted by returning plasma ions (as those ions can interact with the peaks on their way to the valleys) and therefore, it takes them longer to be etched away. If this mechanism is indeed the one occurring during the 50 hr test, it can explain the different temperature gradients observed in the sputtered gold sample, the range was 0.094 eV.

The peaks before and after sample exposure to the cathode plasma are shifted relative to each other and do not align perfectly with the peak location from the database, see Table 1. Small shifts of this scale are either due to different stress states of the sample or lack of calibration in the instrument. The sample was manufactured by hot isostatic pressing (HIP) and after the exposure to the plasma the sample was subject to a fast cool down. It is then reasonable to believe that different stress states appear in the sample before and after plasma exposure, which could explain the peak shifts. Another feature worth mentioning is the double peaks that appear at some peak locations, for example, in Fig. 21 at the (111) crystal location. This is most likely due to the lack of perfect monochromatic X-ray emission by the XRD X-ray source combined with the long integration times.

In Fig. 21 we show the comparison of the intensities of the three most significant crystal orientations in the XRD analysis for the sample before and after plasma exposure along with the three best quality database points we could find for \( \text{LaB}_6 \) in the ICDD database. Each set has been normalized to the peak intensity of its own (110) peak. The XRD relative intensities between peaks for a powder sample that show no texture is a fingerprint for each material.

The relative intensity between crystals (111) and (100) based on data from the ICDD database is

\[
\frac{I_{(111)}^{\text{mean}}}{I_{(100)}^{\text{mean}}} = 0.71 \quad \text{(see Table 2), for the test article case prior to exposure is} \quad \frac{I_{(111)}^{\text{bp}}}{I_{(100)}^{\text{bp}}} = 0.96
\]

and after is \( \frac{I_{(111)}^{(111)}}{I_{(100)}^{(100)}} = 3.3 \). The discrepancy of this ratio for the test sample before exposure is 36 % relative to the mean relative intensity from the ICDD data. In the case of the sample after the exposure it is 361%. The difference in this ratio between the sample after exposure and the ICDD data is a consequence of the development of a non random crystal distribution at the surface of the sample, in other words, a texture has developed. Similar results can be found by examining the rest of the XRD spectrum.

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EBSD
In the downstream area analysed (see Fig. 7), there is a higher portion of the data points (black areas on the image) that do not match any of the six crystalline structures listed, compared to the portion exhibit on the upstream area. There are three possible explanations for this phenomena: first, the pattern could belong to a crystalline phase that we are not aware of, and therefore, we are not comparing it with the correct pattern set from the database; second, there is no pattern due to the presence of an amorphous substance at the surface. Third, this data could be due to the lack of flatness that we observed in the morphology of the surface on the downstream end of the sample, see Fig. 8. In this case, the Kikuchi patterns exist but cannot reach the EBSD detector, either because they are out of focus, or because the projection lies outside the detection area of the apparatus. We do not think the amorphous hypothesis is correct because the amorphous patches that appear in the crevices of the sample have a characteristic length on the order of ∼5 µm and the size of the unidentified regions in the EBSD image data is on the other of ∼50 µm. We believe the effect of the surface morphology on the back-scattered pattern is the most promising explanation. The fact that the upstream map contains significantly fewer data points without match compared to the downstream one and the correlation with surface roughness, suggest that the change in morphology is behind the increase of unidentifiable data-points.

Morphology

The observed roughness at the downstream end of the insert suggests that the effective emissive area has increased. Cathode operating temperature depends on the total thermionic emission for the given cathode operating point, which in turn depends on the size of the emitting area. An increase in insert surface area could therefore result in a reduction of the cathode operating temperature. To address the contribution of surface roughening to the observed lower operating temperature at steady state, we sought to quantify the insert surface increase following plasma exposure. Based on the morphology at the roughest end of the insert observed by SEM, we assumed a simplified model where the surface is composed of square pyramids, see Fig. 9. The pyramid height (h in Fig. 9) is estimated from the distance between valleys and peaks detected by profilometry analysis Fig. 18. The maximum value for this distance is 12 µm. In order to dimensionalize the size of the pyramids (a in Fig. 9), we used the profile of the surface along line 3, Fig. 10. The profile of the downstream end of the insert shows that the pyramids side length is bigger than 30 µm. Assuming h= 12 µm and a= 30 µm, the surface area is 1.28 times the nominal area; a=20 µm and h=15 µm would result in a 1.8 times increase of the nominal area. The latter assumption is a large overestimation, especially given that sharp roughening is only present in the downstream end of the insert. When the effective area is doubled, the expected reduction of temperature is no more than 70 °C. Therefore, while surface roughening may contribute to lower operating temperatures, it cannot fully explain the cathode thermal behaviour at
steady state.

Collectively, the temperature evolution of the LaB₆ hollow cathode and the work function measurements with UPS presented in this study suggest that 50 hr exposure to the internal plasma of a hollow cathode improves the work function of polycrystalline LaB₆ with respect to the work function of the material prior to the exposure. Specifically, the work function measurement was performed in the test article at room temperature after exposure to the atmosphere, which suggests that the effect of the interaction of the plasma with the surface is permanent (the work function reduction is present even when the sample is not interacting with the plasma). The permanent reduction of the work function explains the different thermal transient behavior observed in our previous work¹ between a sample exposed to the plasma after manufacturing and a sample that has been exposed for a significant period of time.

In addition, we have learned that in the downstream end of the cathode, where the work function measured is the lowest, LaB₆ crystal faces have been exposed, as evidenced by SEM image of that area showing a faceted morphology. Furthermore, according to the XRD data Xe plasma creates a crystallographic texture at the LaB₆ surface. In summary, data showed that plasma-exposed insert surface consists of exclusively LaB₆, displays a faceted morphology and a crystallographic texture, and has a permanently reduced work function. Taken together, these results suggest that plasma-surface interaction induces a preferential exposure of LaB₆ crystal orientation associated with reduced work function (with respect to the vacuum value of 2.66 eV). From the thermodynamic point of view, given that those crystals survived the interaction with plasma ions, they should be among the most highly stable crystals of LaB₆. Therefore, we anticipate that these crystals correspond to the lowest surface energy crystals of LaB₆, which according to a DFT study⁵ are the crystals which exhibit the lowest work function of the material. The results of our study are in agreement with that theory.

With respect to the presence of LaB₄ in the sample after plasma exposure, both EBSD and XRD analyses show no evidence of this compound. However, there is a possibility that LaB₄ exists while the cathode is in operation and it transitions to LaB₆ as the cathode cools down. In this work we cool down the cathode as fast
as possible with the goal of freezing the chemistry at the surface of the insert. It will be of interest to model
the kinetics of the transformation between LaB\(_4\) and LaB\(_6\) and compare it with the cool down rates of this
work in order to understand the probability of the existence of LaB\(_4\) prior to the cathode being shut down.

It is advisable to gain more insight into the La recycling hypothesis\(^1\) in order to experimentally confirm
that La gets recycled. We showed that short thermal transients occur as the operating condition of the
cathode is changed.\(^3\) Since the timescale of these transients is only few minutes, it is unlikely that they
are caused by the crystallographic evolution of the insert surface. However, these short transients could be
explained by a dynamic redeposition of ionized lanthanum which depends on the transport of this species by
the specifics of the plasma distribution for each operating point of the cathode. In this case, the forced cationic
termination that the recycled La would exert in the crystals of LaB\(_6\) could be behind the aforementioned
short time scale thermal transients. Those terminations would not be stable without the constant recycling of
La, as the naturally terminated boron crystals would reappear when the operating condition of the cathode
changes the plasma structure in the internal domain of the cathode and therefore affect the recycling intensity.
The formation of LaB\(_4\) could also explain the short thermal transients only if LaB\(_4\) exhibits a lower work
function than LaB\(_6\) and at the same time, the kinetics of the transformation towards LaB\(_6\) are on a short
timescale, one that matches the observations of this discussion. Additional work should be done to confirm
that La is effectively recycled in the insert plasma.

Acknowledgments

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Institute of Technology. Portions of the research described in this paper were carried out at the Jet Propulsion
Laboratory, California Institute of Technology, under a contract with the National Aeronautics and Space
Administration.

References

7Thompson, R., “Production, Fabrication and Uses of Borides,” The Physics and Chemistry of Carbides, Nitrides and
Appendix 1: tables

<table>
<thead>
<tr>
<th>Crystal face</th>
<th>$PL_{\text{ICDD}}^{\text{mean}}$</th>
<th>$PL_{\text{ICDD}}^{\text{std}}$</th>
<th>$PL_{bp}$</th>
<th>$PL_{ap}$</th>
<th>$E(PL_{bp})$</th>
<th>$E(PL_{ap})$</th>
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$PL_{\text{ICDD}}^{\text{mean}}$: peak intensity mean value based on ICDD\textsubscript{006,0401}, ICDD\textsubscript{034,0427} and ICDD\textsubscript{065,1831}

$PL_{\text{ICDD}}^{\text{std}}$: peak intensity standard deviation value based on ICDD\textsubscript{006,0401}, ICDD\textsubscript{034,0427} and ICDD\textsubscript{065,1831}

$PL_{bp}$: peak location before plasma exposure

$PL_{ap}$: peak location after plasma exposure

$E(PL_{bp}) = PL_{bp} - PL_{ICDD}^{\text{mean}}$

$E(PL_{ap}) = PL_{ap} - PL_{ICDD}^{\text{std}}$

Table 1: XRD diffraction peak location analysis. Table shows location values (in degrees) of XRD diffraction peaks for LaB$_6$ as reported in the literature, and as estimated in our measurements on the test sample before and after plasma exposure.
<table>
<thead>
<tr>
<th>Crystal face</th>
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<th>$I^\text{std}_{\text{ICDD}}$</th>
<th>$R^{(100)}_{\text{ICDD}}$</th>
<th>$I^\text{bp}_{(100)}$</th>
<th>$I^\text{ap}_{(100)}$</th>
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<th>$E% \left( \frac{I^\text{ap}<em>{(100)}}{I^\text{bp}</em>{(100)}} \right)$</th>
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$I^\text{mean}_{\text{ICDD}}$: peak intensity mean value based on ICDD\text{006,0401}, ICDD\text{034,0427} and ICDD\text{065,1831}

$I^\text{std}_{\text{ICDD}}$: peak intensity standard deviation value based on ICDD\text{006,0401}, ICDD\text{034,0427} and ICDD\text{065,1831}

$I^\text{bp}_{(100)}$: peak intensity before plasma exposure

$I^\text{ap}_{(100)}$: peak intensity after plasma exposure

$E(X) = \left( \frac{X - R^{(100)}_{\text{ICDD}}}{R^{(100)}_{\text{ICDD}}} \right) \times 100$

$R^{(100)}_{\text{ICDD}} = I^\text{mean}_{\text{ICDD}} / I^\text{mean, (100)}_{\text{ICDD}}$

Table 2: XRD diffraction peak intensity analysis. Table shows intensity values of XRD diffraction peaks for LaB$_6$ as reported in the literature, and as estimated in our measurements on the test sample before and after plasma exposure.
Appendix 2: additional figures

Figure 11: Vacuum chamber used in the experiment.

Figure 12: UPS spectra for the LaB$_6$ test article after plasma exposure at location $\bar{z} \sim 0.884$ (see Fig. 6) obtained with aperture $110 \times 110 \, \mu m^2$. 

Work function = 3.313 eV
Figure 13: Thermal transient during shut down.

Figure 14: Cathode operational parameters measured during 50 hr test: discharge voltage and current, and keeper voltage.
Figure 15: Cathode operational parameters measured during 50 hr test: chamber pressure and Xe mass flow rate.

Figure 16: Test sample (part B) after the 50 hr test. Sample shows carbon contamination in most of its internal area.
Figure 17: Surface profiles acquired before plasma exposure

Figure 18: Surface profiles acquired after plasma exposure
Figure 19: Test sample XRD spectra results. Comparison with LaB$_4$ database ICDD 00-024-1015

Figure 20: Test sample XRD spectra results. Comparison with LaB$_6$ database ICDD 00-006-0401
LaB₆ cathode sample analysis (background subtracted and normalized to 110)

Figure 21: Test sample XRD spectra results. Intensity comparison.