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Key design and operation factors for high performance of C12A7:e- based cathodes

A. Post¹, J. F. Plaza¹, J. Toledo¹, D. Zschätzsch², M. Reitemeyer², L. Chen², A. Gurciullo³, A. Siegel⁴, P. J. Klar², P. Lascombes³, and B. Seifert⁴.

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¹ Advanced Thermal Devices, C/Villaconejos 4, 28925-Alcorcon, Madrid, Spain

² Institute of Experimental Physics I, Justus-Liebig-University, Hessen, 35392 Giessen,

Germany

³ Exotrail, 3 Rue Galvani, 91300 Massy, France

⁴ FOTEC, Viktor Kaplan-Straße 2, 2700 Wiener Neustadt, Austria E-mail: apost@atdevices.com

Abstract. This work, based on an EU-funded project (NEMESIS), is summarising some of the results from the project activities on the research and development on electride-based cathode technology compatible with all kinds of electric propulsion (EP) systems requiring neutralization or electron emission. Further information describing in detail the performed tests and captured measurements can be found in the referenced documents of each section. Different cathode architectures and several emitter configurations with traditional and with alternative propellants are being developed and tested within the project, all of them using C12A7:e- electride material as thermionic electron source. Findings and conclusions derived from these multiple designs are allowing to figure out some of the key factors that determine the best performance of C12A7:eelectride based cathodes. In this work, a discussion of some of these key design and operation factors will be presented based both on the material characterization parameters, and on the performance tests carried out for the different cathode designs.

1. Introduction

In most materials, electrons are either associated with specific atoms or molecules, or are delocalized as in a metal. Electride materials are ionic compounds in which some electrons replace the negatively charged ions and serve as anions. The EU-funded NEMESIS project is developing cathode technology, based on electrides, that is compatible with all kinds of electric propulsion systems that require a neutralizer. The C12A7:e- neutralizer technology posits high reliability, compatibility with alternative propellants, as well as lower power consumption on satellites.

One of the objectives is to demonstrate the performance improvements that the novel thermionic emitter material C12A7:e- can bring into the neutralizer technology for space electric propulsion systems. Improving the performance of on-board EP devices will accelerate the availability of simpler and cheaper platforms for small satellites, thus improving the competitiveness and strength of the European space industry, with associated employment and scientific level increase. It would even pave the way for enabling brand new exploration, scientific and commercial missions not yet available due to actual constraints of traditional thermionic emitters technology.

Material properties of the electride C12A7:e- are exceptional for application in ceramic-based neutralizers or cathodes. Nevertheless, the challenge is to fully transfer the theoretically ideal material properties of C12A7:e- to real neutralizer devices in order to fully make use of its potential. This would allow to achieve better performance and reliability, and become a disruptive force in the cost-driven

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satellite market. The interdisciplinary *NEMESIS* consortium addresses the full sequence steps from material synthesis to device design, fabrication, integration and testing. All these steps are connected and being permanently validated within the consortium [1].

2. Materials selection criteria for C12A7:e- based electron emitter devices

In order to determine the most suitable materials and structures for the construction of cathode prototypes based on C12A7:e- electride as emitter material, the most relevant physical characteristics of the said material have to be analyzed in a first step.

In this section we will discuss some of the criteria, based on C12A7:e- parameter characterization, that have to be taken into account to select the materials to be part of these type of devices.

When working at high temperatures, above 600°C, it is very important to care about the thermal expansion coefficient (TEC) of the materials that will be in contact with the electride. In our case, we have to match the C12A7:e- electride TEC with a value of 6.1 x 10^{-6} W/m K.

At these high temperatures it is also important to pay attention to the chemical reactions of the electride with other materials, and to parameters like the oxidation enthalpy of the metals to be used in order to prevent metal oxidation that could produce undesired electrical insulation effects between the electride and the metal. Also, the combination of the TEC of materials, plus the evaporation rate level in vacuum, and the oxidation enthalpy relative to the electride, lead at the end that only few metals are suitable to be used in contact with the C12A7:e- electride material.

Other thermal and electrical parameters of the electride, like the thermal radiation emissivity, the thermal and electrical conductivities, and the heat capacity, are also important to foresee the thermal and electrical response of the C12A7:e- within the cathode device.

As an example, the C12A7:e- heat capacity together with its semiconductor behavior with a positive electrical conductivity coefficient with temperature, in combination with the low thermal conductivity, leads to a positive feedback loop that promotes hotspots and thus leads to instabilities at high temperatures. [2].

The thermal radiation emissivity coefficient determines the heating power consumption and the infrared radiation released to other elements of the cathode. In our case, C12A7:e- presents a high coefficient above 0.9. This will require high heating powers to bring the material to its operation temperature, and it will also require designing the appropriate radiation confinement structures.

The above parameters have been studied to select the most appropriate metals and insulator material necessary for proper operation of the cathode under actual space conditions.

3. Exposure of C12A7:e- to alternative propellants

In order to check the behavior of the electride material for different applications, an analysis of alternative propellants compatibility with C12A7:e- was carried out at *JLU Giessen* [3] [4]. The tests were performed for Krypton, dirty Xenon (oxygen at low partial pressures), Bismuth, Indium, and Iodine. In the case of Krypton and dirty Xenon, a direct exposure to gas flows in the vacuum chamber was applied. For Bismuth and Indium, pellets were deposited on top of a C12A7:e- disc surface inside a crucible and then heated at 350°C for 60 minutes in vacuum. Both Bi and In are ln liquid state at these conditions, and this ensures these material spread over the surface with a complete coverage of the electride sample with a negligible evaporation rate.

For Iodine, the electride material was subject to two consecutive contamination processes. The first process involved a short heating of the electride sample with solid iodine in a previously evacuated tube to moderate temperatures and a subsequent settling process over a week. The second exposure involved a higher and longer applied temperature with the same settling time.

Subsequent material characterization with Raman spectroscopy and X-ray photoelectron spectroscopy (XPS) could not find remnants of neither Bismuth nor Krypton exposure on the electride samples.

Indium and Iodine, however, could be detected at the surface by XPS, especially for the second iodine treatment. This was also confirmed by Scanning electron Microscope (SEM) surface imaging, where an altered surface roughness was found (see Figure 1). Despite that, the Raman spectra of all samples remain nearly identical. Taking this into account, together with the contaminant decrease with rising etching time that was observed in XPS. It can be concluded that the occurred exposure mainly affected the material surface and not its overall structure integrity.

Based on the previous results, all analysed alternative propellants, except dirty Xenon due to oxygen contamination, seem to be compatible with the electride material. Solely for dirty Xenon exists a limitation since high oxygen partial pressures at high temperatures lead to strong C12A7:e- damages. For common Xenon impurities, the extent of this limitation has to be further studied.



Figure 1. Surface images for samples untreated (left), treated with Iodine (center) and with Indium (right) with a Scanning Electron Microscope (SEM).

4. Results achieved in performance tests

4.1. Performance tests in vacuum.

Thermionic emission tests on manufactured C12A7:e- disc samples have also been initially performed in high vacuum conditions. These tests provided values for the work function in the 1.4-2.4 eV range. On its side, Ultraviolet Photoelectron Spectroscopy (UPS) and XPS gave values between 1.9-2.8 eV. Such variations are caused by the accuracy of the technique employed, the physical conditions of the surface of samples and the external electric field applied in some tests.

These measurements of the work function are basically in agreement with the 2.4 eV value previously reported in literature [5-6], and with the 2.38 eV value obtained by a monochromatic laser photon source. This last technique determines precisely the energy required to extract electrons from the surface of the material without externally applied electric field and/or sample heating. In our measurements, the wavelength was 520 nm, which corresponds to a work function of 2,38 eV [2].

The electron thermionic emission currents from the C12A7:e- samples were measured by *Exotrail* company to determine its effective work function. The experimental data are represented in figure 2, and figure 3 shows the best fit of the experimental IV data of figure 2 to the classical Richardson-Dushman equation [7]. This best fit gives a value of $Ø_0 = 2.41$ eV for the work function and of D = 1.8 A /(cm2 K2) for the Richardson constant for the C12A7:e- electride sample.

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Figure 2. I/V curves of the thermionic emission raw data from a C12A7:e- disc sample.



Figure 3. The linear fit of the raw experimental data of figure 2 to the classical Richardson-Dushman law.

Despite its low work function, the small value for D leads to small thermionic emission currents, as it has been verified by all NEMESIS consortium partners. Nevertheless, this limited emission level is not so low when operating with gasses. The table 1 shows the difference between operating in high vacuum and high temperature versus operating in the presence of ions of a plasma.

These measurements were taken using the same thermionic emission test set-up provided with an active heater to reach the operation temperature of 950 °C. One measurement was performed under high vacuum and the other measurement in presence of Ar with a mass flow of 10 sccm. All tests were performed in the same vacuum chamber at similar conditions listed in Table 1 where P_{heater} is the power consumption of the heater system, V_a is the voltage applied in the anode and I_a is the current collected in the anode.

4.2. Performance tests in presence of gas.

As it can be observed in Table 1, the anode current and the performance ratio are multiplied by a factor of approximately 15 in the presence of a gas. With all the parameters characterized, their implications in the design of the cathode devices, and together with the outcome of the analysis of exposure of C12A7:e- to different alternative propellants, several cathodes with different architectures are developed within the project. Out of them, a hollow cathode, a heaterless neutralizer, and a miniature neutralizer cathode are under development and test for operating with iodine.

Table 1. Emission performance comparison in vacuum and in presence of Ar				
Atmosphere	Pheater (W)	Va (V)	I _a (mA)	I _a /P _{ck} (mA/W)
Vacuum	160	100	1.2	0.008
Ar	160	100	20	0.125

In this section, one of the devices developed by *ATD* is described, together with the results of

performance test under different operation conditions. In this case, the cathode is a heaterless neutralizer working at low temperatures. A conceptual scheme and a description of the main characteristics of the cathode are represented in Figure 4. The second electrode used for plasma ignition, is denominated as keeper by analogy to hollow cathode terminology.



Figure 4. Scheme of the heaterless neutralizer designed and implemented for performance tests.

The performance measurement tests presented hereafter were obtained using the same vacuum chamber, and test set-up cathode prototype configuration, that is described in Tables 2 and 3.

Table 2. Main characteristics of the vacuum chamber and control equipment.				
	300x300x350 mm size Turbo molecular pump Edwards EXT255H			
Vacuum chamber				
	Vacuum pump Alcatel			
	Baseline pressure to 10 ⁻⁷ Torr			
	Connections for 9 thermocouples			
	Pico-ammeter (Keithley DDM 6500)			
Control equipment	DB9 feedthrough connection for 9 analog signals			
	Two current sources (100 A, 22.3 A)			
	High voltage power supply 300 V			

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Table 3. Performance test conditions		
C12A7:e- sample	25.4 mm diameter and 2 mm thickness	
Cathode voltage (V _c)	150-300 V	
Gas	Ar and Xe: from 1 to 50 sccm mass gas flow	
Thermocouple	Type K connected at the base of the sample	

As it will be presented in the following figures, the anode current (I_a) was obtained as a function of the anode voltage (V_a), gas flow and cathode power (P_k) parameters. The anode current (I_a) was measured for different anode voltages (V_a), holding the cathode electric power ($P_c = V_c \times I_c$) constant at fixed mass flow rates. First, the electride sample was warmed up to 250 °C to avoid the instabilities observed when the discharge was triggered below 200 °C. Figure 5 shows the anode current as a function of its anode voltage for constant 0.9 sccm of Xenon and 1.5 sccm of Argon, which are the values where a stable operation mode of the cathode was reached. For V_a between 0 and 30 volts the anode current for Argon ranges 20-120 mA, and 2-28 mA for Xenon. As it can be seen in Figure 5, an anode current of 20 mA was obtained using 1.5 sccm of Ar at zero anode voltage and 100 mA when applying 20V.



Figure 5. I/V characterization for the C12A7:e- emitter operating in the heaterless neutralizer with 0.9 sccm Xe (left) and 1.5 sccm Ar (right).

Table 4 shows the performance of the heaterless neutralizer, with C12A7:e- as electron emitter, working at different Xe and Ar mass flows with 30 W cathode power and 20 V anode voltage. As Table 4 indicates, the I_a/P_c ratios obtained with Xe and Ar are ranging from 1 to 3 mA/W.

Mass flow	P _c (W)	V _a (V)	I _a (mA)	I_a/P_c (mA/W)
1.5 sccm Ar	30	20	99.6	3.320
10 sccm Ar	30	20	110	3.367
0.9 sccm Xe	30	20	26	0.867
50 sccm Xe	30	20	31.9	1.063

Table 4. Heaterless neutralizer performance test results working

These tests show the great possibilities of C12A7:e- for designing cold cathodes for neutralizers. However, there is room for better performance ratios by recent design improvements presently under study in the NEMESIS project.

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Figure 6 illustrate the promising performance results achieved by the new configurations using an improved heaterless neutralizer cathode design (patent pending) and some variants in C12A7:eelectride material production processes and treatments. In Figure 6 are represented the I-V curves obtained following the scheme presented in Figure 4, and four different configurations which are the combinations of two design variants and two variants for C12A7:e- electride synthesis process that are presently under tests. In these measurements, a mass flow of 10 sccm of Ar was used together with a grounded (0 V) anode, and approximately 10 W consumed by the cathode.



Figure 6. I/V characterization curves of 4 new configurations with the improved heaterless cathode.

As it can be observed in Tables 5 and 6, an excellent I_a/P_c ratio of over 6 mA/W was obtained. In addition, a minimal keeper loss with an I_{keeper} lower than 2% of $I_{cathode}$ was obtained, even with using 0V in the anode, and providing anode currents even with negative V_a voltages.

				inproved incatoritopp	
Configuration	Vcathode (V)	Icathode (mA)	I _{keeper} (mA)	I _{anode} (mA)	P _c (W)
1	164	59.2	0.95	58.25	9.7
2	156	59.3	0.11	59.19	9.3
3	160	60.4	1.18	59.20	9.7
4	160	60.6	0.11	60.50	9.7

 Table 5. Performance test results for four new configurations with the improved heaterless cathode design

Table 6.	Performance ratios for 4 new configurations with the	
	improved heaterless cathode design	

Configuration	I _a /P _c (mA/W)	Ia/Ic (%)
1	6.0	99.4
2	6.4	99.8
3	6.1	98.0
4	6.2	99.8

As previously commented, these last results will be also replicated and confirmed by different *NEMESIS* project partners. Additional proposals of possible additional improvements starting from the basic heaterless neutralizer cathode design are envisaged.

5. Conclusions

In this work we have studied and analyzed some key factors involved in the design of C12A7:e- based cathodes. Different critical parameters were established and optimized to achieve high performance C12A7:e- based cathodes.

Also, alternative propellants compatibility have been analyzed, and almost all alternative propellants studied with C12A7:e- seem to be compatible with the electride material. In addition, long term tests will be performed within the NEMESIS project in order to obtain a hollow cathode, a heaterless neutralizer, and a miniature neutralizer cathode operating with iodine.

As it was described, the C12A7:e- material presents some drawbacks when operated with pure temperature induced electron emission. Nevertheless, this is not the case when operating with gasses.

Finally, the excellent results of this heaterless C12A7:e- based neutralizer working at low temperatures were presented. The experimental results discussed above can be potentially improved incorporating small cathode design variants and samples coming from more refined electride material processing. Some are presently under study by different partners of the present project, with very promising initial test results in terms of performance ratios, where I_a/P_c ratio is above 6 mA/W and keeper current losses are below 2% of the cathode current.

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