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Ammonia fuelled space electric propulsion systems using C12A7:e- electride as electron emitter

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Abstract. Given the significant changes taking place in the geopolitical global situation, and the derived supply chain issues for some traditional electric propulsion propellants like xenon, alternative propellants issue is perceived as a strategic topic to tackle, and ammonia (NH_3) is becoming one serious candidate. Ammonia is increasingly being investigated to extend green hydrogen use by overcoming the storage and transportation issues of hydrogen. Ammonia characteristics like its superior energy density and low temperature and/or pressure needs for storage (10 bar at 20ºC for liquid ammonia), make it very valuable for simplified unexpensive energy storage and transportation, and these characteristics makes it also especially suitable for on-board spacecrafts electric propulsion purposes. Based on our research activities on ammonia generation and dissociation processes with C12A7:e- electride as catalyst, this work will describe the most relevant characteristics and properties associated to the advantages of using the cheap and abundant ammonia, and will also present and discuss the results of the first successful tests performed with ammonia as fuel for a C12A7:e- electride based neutralizer, including relevant endurance tests in operation conditions. Additionally, the dual application as propellant and on-board energy generation system of ammonia will also be discussed.

1. Introduction

The current geopolitical crisis affects some elements of the supply chain and compromises recent advances made in Electric Propulsion (EP) [1,2]. In special xenon and krypton, and even neon, are affected due to their increasingly high costs. Looking at the future, it is necessary to guarantee the supplies availability. In this regard, the use of gases based on abundant and cheap elements, or compounds with a high efficiency in weight and volume which are easy to transport, is critical. These are special requirements for small satellites and probes where the use of alternative propellants, as iodine, is being studied [3,4].

In this case, ammonia (NH_3) meets all the above criteria making it a serious candidate to become the ideal propellant for the future in many scenarios. Nonetheless, the materials compatibility and the efficiency regarding the substitution of heavy gases, such as xenon or krypton are the main issues to be solved.

Many possible applications of ammonia have already been studied [5–9], including its use as propellant for space propulsion applications [9,10]. Additionally, the use of the electride has also been applied for the synthesis and decomposition of ammonia [16–19]. In this work, the use of ammonia for neutralizers and thrusters will be studied. In this case, the C12A7:e- electride, hereinafter named as electride, will act as the emitter material for the cathode, able to provide an electron current emission when it is properly operated [11]. The electride is a doped ceramic semiconductor which reaches an electron concentration up to levels close to $2.3\cdot10^{21}$ cm^{-3}, and with a work function of approximately 2.4 eV [3,9–

12]. This material is synthetized from a wide-bandgap insulator with a reduction process at high temperature where the O_2^{2-} ions present at the crystal cells of the insulator are substituted by electrons. By means of this process, the electride can be dopped with different electron concentration levels and can behave, depending on the doping levels, as a semiconductor or even as a metallic conductor with high conductivity at room temperature. The electrons injected by this process occupy the conduction band and migrate through the electride crystal by tunnelling. This electride material can operate at low temperatures, it is chemically inert, and it is produced within Europe with locally available unexpensive materials.
Due to these characteristics, the use of the electride as cathode is the ideal solution for the application in neutralizers and thrusters where ammonia is used as the propellant.

The following sections describe the ammonia winning factors regarding the supply chain issues, the synthesis methodologies, and its efficiency in weight and volume for storage and transportation aspects. Also, the use of ammonia in neutralizers and thrusters will be described, together with a summary of the main issues and results.

2. Ammonia winning features

2.1. Ammonia supply chain

Ammonia has a complete regulation on transport and industrial use and is a well-known and proven compound, and is one of the chemical compounds most used in industry, especially in its application for fertilizers production [9]. On the other hand, decarbonization targets are boosting the use of ammonia for hydrogen (H_2) storage and even for its direct use as fuel in ships [5,6]. This implies the need of large growth in the worldwide production capacity to guarantee supply.
Haber-Bosch ammonia synthesis process, which requires large plants and continuous process [8,20], is being adapted for the use of green H_2, coming from electrolyzer devices, and replacing natural gas as the primary process input. In addition, new processes based on recent catalysts allows smaller production plants, with lower investment entry barriers, and allow intermittent processes to pace to renewable energy generation production sources such as solar or wind. These would imply the entry of many new ammonia production players based on renewable energy generation assets.
Therefore, considering the large volumes of ammonia required by many industries like the fertilizers production or the mentioned marine transport, and the need of decarbonization in its production process, high level of investments and research effort is envisaged in new green NH_3 synthesis processes.

2.2. Ammonia synthesis from H_2 and N_2

Hydrogen (H_2) is the most abundant element in the universe, and nitrogen (N_2) is close to 80% of the air composition. They both are the key elements to the formation or synthesis of ammonia. Despite the above-mentioned considerations about the supply chain and the risk of shortages because of the increasing demand, the price trend for ammonia, historically remaining bellow 0,6 €/kg, is still contained. Even with the recent natural gas price increase, the price remains less than 1.5 €/kg, and in retail the prices are between 3 €/kg and 6 €/kg. The big competition expected with new ammonia providers with the production process simplification and the entry barriers reduction, will to our understanding keep the price levels of ammonia at reasonable levels close to the present ones.

2.3. Ammonia efficiency regarding weight and volume (storage and transport)

Ammonia, gas at 1 bar and 25ºC, has a very useful property since it liquifies at -33.4ºC at 1 bar or 25ºC at 10 bar. The change of state means around 898 mass ratio from liquid to gas or, in other words, an equivalent compression about 898 bar for a comparable gas that does not liquify at the above pressure-temperature parameters, such as xenon, krypton, argon of hydrogen (see Table 1).

Table 1. Conditions of liquid ammonia

-33.4ºC at 1 bar or 25ºC at 10 bar	
Density (Liquid) (g/l)	682
mol/l	40.12
Gas (l)	898.64
Compress ratio Liquid/gas	898.64

As indicated in Table 2, ammonia has a molecular mass of 17 g/mol which it is excellent for plasma-based neutralizers where is needed a low mass for a significant electron emission, but on the other hand, is not ideal for thrusters since it requires more ions for a comparable thrust.

The comparisons with xenon, krypton and argon described in Tables 2-3 and in Figure 1, show a significant advantage of ammonia in volume or pressure for the same mass. On the other hand, no boiling process, or what is the same, no energy is necessary for gas disposal from liquid ammonia.

Table 2. Mass comparison 1 l, 10 bar

Propellant	Mol [g]	Mass [g]	Mass mol rate	Notes
Ammonia (NH_3)	17	682	1	No energy needed
Xenon (Xe)	131.3	58.62	7.72	
Krypton (Kr)	83.8	37.41	4.93	
Argon (Ar)	39.95	17.83	2.35	
H_2 Equivalent	2	0.89	0.12	
H_2O	18	1000	1.06	Needs energy (Evaporation and/or electrolysis)

Table 3. Pressure required at constant volume of 1 l for storing 682 g of mass

Propellant	Pressure [bar]	
Ammonia (NH_3)	10	For equivalent mass
Xenon	116.35	
Krypton	183.30	
Argon	382.40	
H_2 Equivalent	1,347.95	For equivalent energy
H_2O	N/A	Needs energy (Evap. and/or electrolysis)

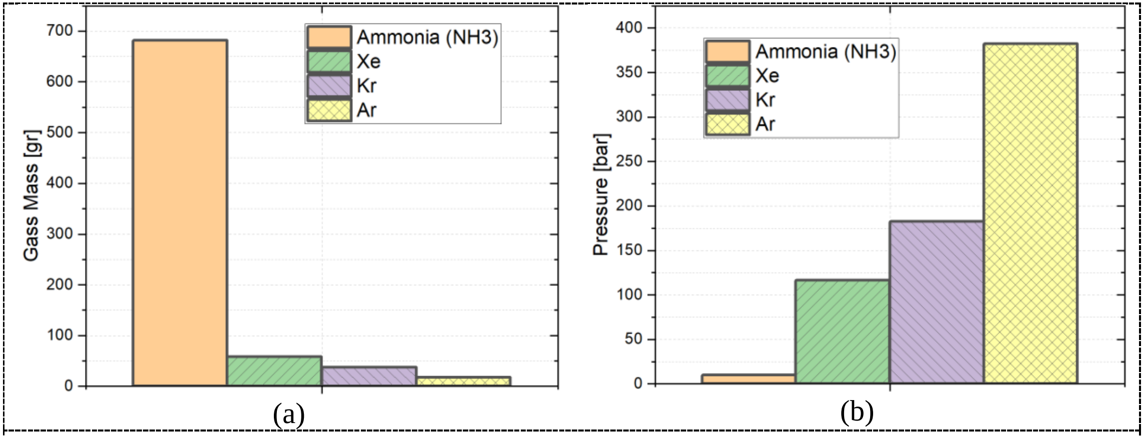


Figure 1. (a) Gas mass (NH_3, Ar, Kr, Xe) contained in 1 l at 10 bars. (b) Pressure needed to get the same mass than 1l Ammonia at 10 bar for Ar, Kr and Xe

2.4. *Liquid Ammonia energy (H_2) storage*

In addition, ammonia has a high H_2 content, 17.6% in weight, which means 5.88 kWh/kg or 4 kWh/l. Since ammonia is one of the best H_2 molecular "packer", it is called to play an important role in the decarbonization process. As indicated, ammonia liquifies at -33.4 ºC at 1 bar, or at 25 ºC at 10 bars, that means a gas/liquid compression ratio close to 898. As consequence, ammonia has a high capacity to store gas in a small volume with low pressures and no special cryogenic conditions. As Table 4 and Figure 2 show, it is an ideal candidate for liquid storage and gas propellant. In conclusion, all these parameter values indicate that ammonia can be the future energy storage element of Fuel Cells.

Table 4. Maximum H_2 molecular packaging

	Methane CH_4	Methanol CH_3-OH	Ammonia NH_3	Water H_2O
Mol weight	16	32	17	18
H weight/mol	4	4	3	2
%H in weight	25.0%	12.5%	17.6%	11.1%

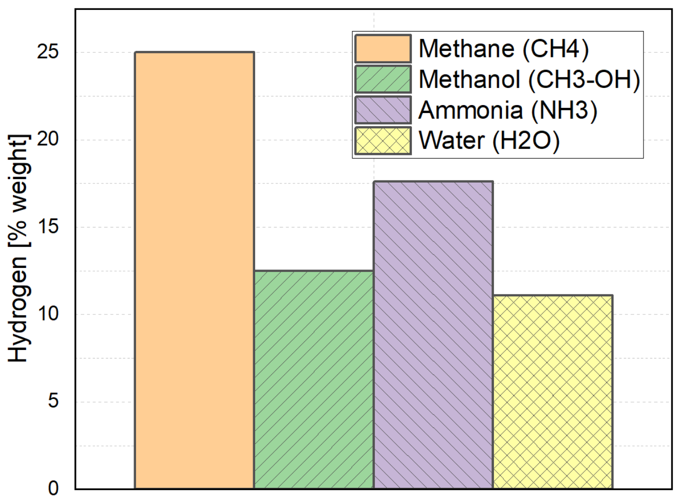
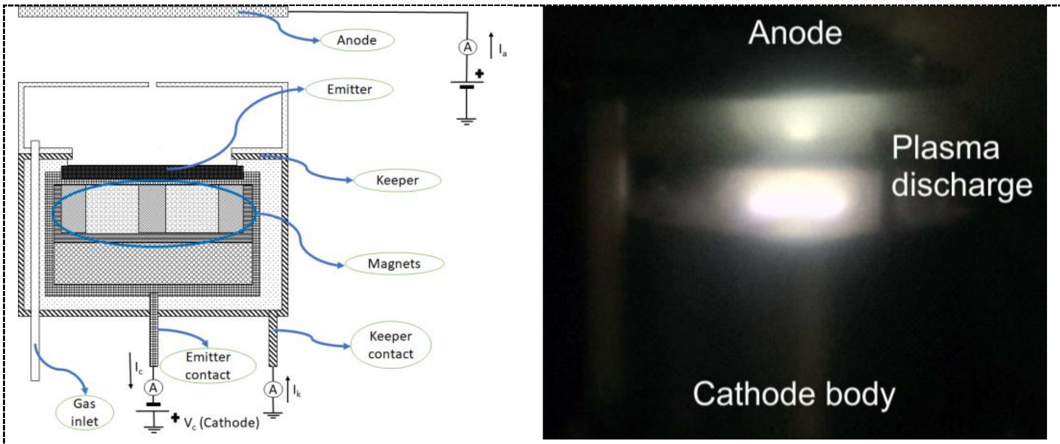


Figure 2. H_2 % contained in weight

3. Ammonia in plasma-based neutralizers

As commented in the introduction section, the use of the electride material as cathode is an ideal solution for the application in neutralizers where ammonia is used as the propellant. In this section, the performance of the electride is verified operating with ammonia, with a gas mass flow of 10 sccm, in a previously described cathode neutralizer [11,13]. Figure 3 shows a scheme of the cathode architecture and a picture of the plasma-based neutralizer under operation with ammonia within a vacuum chanber.



(a) (b)

Figure 3. (a) Cathode architecture developed by ATD. (b) Ammonia Neutralizer plasma

Based on this neutralizer, an initial endurance test of 50 hours was performed with ammonia. In Figure 4 is represented the evolution of the voltage cathode, the anode and cathode current, and the temperature of the sample while maintain a positively bias of 20 V at the anode. As it can be observed, we obtained a remarkable stability and performance obtaining a mean value of 40 mA with 150 V_{rms}. After 24h it is detected a decrease in the cathode and anode current, as well as in the temperature, and some degradation in the sample surface is observed. Nevertheless, there are no chemical reactions with the electride cathode thanks to the low operational temperatures (<300ºC), which prevent NHx- radicals' reactions and generation of compounds such as nitrides and guarantee the operation with ammonia. Even though no chemical deterioration has been observed, additional tests are still being conducted.

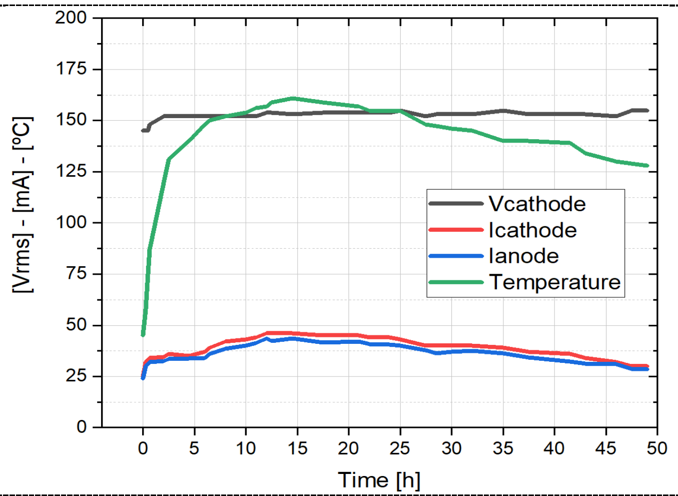


Figure 4. Endurance test for the C12A7:e- emitter with ammonia

To conclude this section, it is important to take into consideration that a 150 cm^3 ammonia tank is approximately equivalent to a volume of 5.6 l of an argon tank and 1.7 l of xenon, when both are at 10 bars. To store the same equivalent mass of argon and xenon, in the same volume of 150 cm^3, a pressure of 382 and 116 bar will be required, respectively. Table 5 shows additional data for mass and volume comparison of different gases for the application in neutralizers.

Table 5. Mass and volume comparison of different gases for the application in neutralizers

	Ammonia NH_3	Argon Ar	Xenon Xe
Mass flow (sccm)		2	
Anode current (mA)	35	40	30
Moles/s		$1.49\cdot10^{-6}$	
Molecules (atoms)/s		$8.96\cdot10^{17}$	
Max current with 100% ionization (mA)		143.32	
Electron in anode versus gas molecules	24.4 %	27.9%	20.9%
Gas consumption (g/s)	$2.53\cdot10^{-5}$	$5.94\cdot10^{-5}$	$1.95\cdot10^{-4}$
Autonomy with 100 g (h)	1098	467	142
Volume at 10 bars (l)	0.15	5.61	1.71
Ar and Xe pressure for same NH_3 volume (bar)	-	382	116

4. Ammonia as thruster´s propellant

Regarding the use of ammonia as propellant for thrusters, a complete test campaign is under process. The objective is to obtain real thrust values and to complete reliable models that could be applied in defined scenarios and thruster configurations. In addition, it is being analysed the nature of NH_x ion species, including densities, in order to get the ions concentration and mass. Figure 5 shows a scheme of the thruster using electride in the cathode.

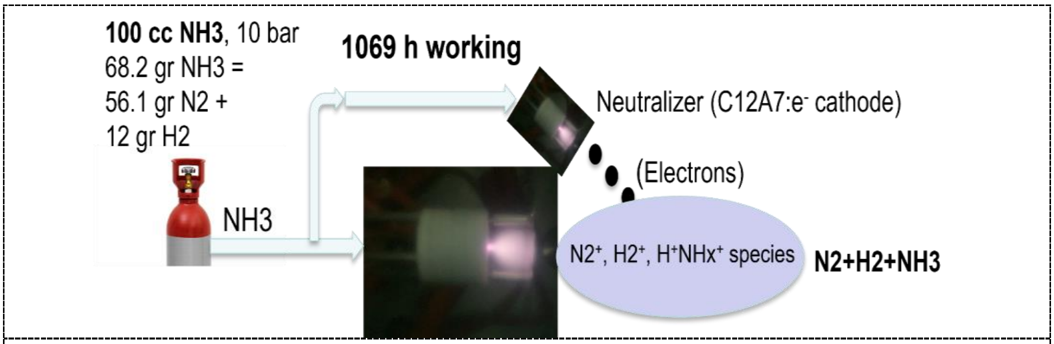


Figure 5. Scheme of the thruster using C12A7:e^- electride as the cathode

Considering the mass mol ratio of xenon and argon versus ammonia (7.72 and 2.35 respectively), and the volume ratio (at 10 bar) of 1.7/0.15 for xenon, and 5.6/0.15 for argon, a 150 cm^3 tank (at 10 bar) would theoretically provide the same thrust than a xenon tank with 1.47 times more volume or pressure or an argon tank with 15.8 times more volume or pressure.

5. Issues

As already indicated, there are still some pending issues regarding the material degradation with the use of ammonia. Table 6 shows a list of possible materials which are compatible with ammonia. These materials are classified into metals and non-metals. Non-metals are materials such as polymers for gaskets, sealing, etc. In the tests performed with the neutralizer and thruster using ammonia as propellant, no chemical degradation was observed with the recommended materials of table 6.

Table 6. Material compatibility of metals and gaskets with ammonia

	Components	*Code	Recommended
Metals	Stainless Steel EN-1.4301 (AISI-304)	A	Yes
	Stainless Steel EN-1.4401 (AISI-316)	A	Yes
	General stainless steel	A	Yes
	Alloy 20 (Ni-Fe-Cr)	A	Yes
	Aluminum	B	No
	Monel (Alloy 400) (Ni-Cu-Fe)	B	No
	Brass (Cu-Zn)	C	No
	Bronze (Cu-Sn)	C	No
	Avoid Cu, Zn, Al		
Gaskets	PTFE (teflon)	A	Up to 200ºC
	E.P.D.M.	A	Up to 150ºC
	Hypalon ® chlorosulfonated polyethylene	A	Up to 140ºC
	Santoprene ® (TPV)	A	Up to 130ºC
	Natural Rubber	A	Up to 90ºC
	Neoprene	B	No
	Buna Nitrile (NBR)	B	No
	Butile	B	No
	Silicon	C	No
	Viton	C	No
	Avoid alkaline hydroxides and strong oxidants		

*Codes: A-compatible, B-care, C-No compatible

6. Conclusions

Ammonia has the special feature to liquify at relatively low pressures (10 bar at 25 ºC). The compression factor Gas/Liquid around 898 allows to get large gas mass storage at relatively low pressures compared with other gases such as argon, krypton and xenon.
Tests carried out so far with C12A7:e- electride based neutralizers show an excellent performance and no degradation of the electride cathodes. Thrusters with NH_3 propellant need to complete the test campaign to validate estimated thrust with real measured thrust, and to complete valid models for thrusters. Also, identified valid materials need additional test campaigns to guarantee their performance over longer endurance tests.
In addition, electride has shown a remarkable performance when operated with ammonia, thus opening the door to the use of ammonia as space electric propulsion alternative propellant, as well as to its use in on-board power systems either as H_2 carrier for H_2 PEM Fuel Cells or for NH_3 direct use in SOFC (Solid Oxide Fuel Cells).

Acknowledgements

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