

Polynitrogen High Energy Density Materials Synthesized by Nonequilibrium Plasma

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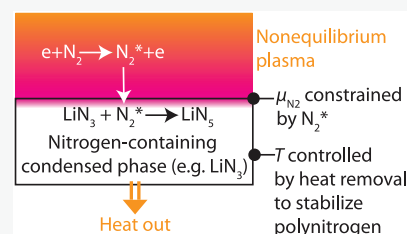
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ABSTRACT: Metal pentazolate compounds that contain 5-nitrogen singly charged anion rings are an interesting class of materials from a thermodynamics perspective. These compounds are believed to be equilibrium phases only at extremely high pressures, and thus, they constitute exotic states of matter at ambient pressure and temperature. Moreover, the energy released by these pentazolate compounds upon relaxation to the equilibrium state at ambient conditions is in the range 1 to 10 MJ per kg, rivaling that of combustion reactions. The synthesis of pentazolates is not an easy task, and there are only two known methods, each of which has significant challenges. The development of new scalable synthesis routes could enable the production of these exotic materials in sufficient quantity to explore their properties more widely beyond the context of explosives and propellants. In this Perspective, it is argued that nonequilibrium plasma is a promising reaction medium for the synthesis of metal pentazolate compounds, for example from the corresponding metal azide and N_2 gas activated by the discharge at low background temperature.



INTRODUCTION

In this Perspective, it will be argued using evidence presented in recently published literature that nonequilibrium plasmas are a promising new reaction medium for the synthesis of polynitrogen high energy density materials (HEDMs), which are an emerging energetic material of interest. The focus in this perspective will be on pentazolate (N_5^-) compounds that are metastable at ambient pressure and temperature. Recent comprehensive literature reviews of this new class of compounds can be found in the publications of Wang et al.,¹ and Wozniak and Piercey.² Materials with a six nitrogen fundamental unit, which have only very recently begun to be explored, such as the black phosphorus structure of polynitrogen^{3,4} and hexazine,⁵ will be omitted for the sake of brevity. Features of nonequilibrium plasma for the synthesis of polynitrogen materials will be discussed. Finally, very recent experimental results from the literature on the synthesis of polynitrogen compounds by plasmas operating very far from local equilibrium will be reviewed.

HEDMs are sought after for their energy storage and release characteristics, but they are different from fuels. A fuel is a material that releases energy, usually heat, through a chemical reaction that typically brings it into equilibrium with the oxygen in the atmosphere. For example, the combustion of alkanes, a major constituent of petroleum-derived fuels, releases approximately 610 kJ per mole of carbon atoms reacted. The elements that the atoms in the fuel are bonded to change during the combustion reaction, going from C–C and C–H bonds to C–O and H–O bonds. Thus, in combustion, there is a fuel (e.g., hydrocarbon) and an oxidizer (e.g., oxygen). The fuel and oxidizer can be separated and then mixed immediately before

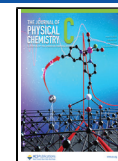
combustion, as in an internal combustion engine, or they can be premixed in the idle state, as in, e.g., a nanothermite^{6–9} or conventional energetic materials such as trinitrotoluene (TNT) or trinitrotriazacyclohexane (RDX). Herein, the term HEDM is used to describe materials wherein energy is stored and released by changes in bonding configurations between nominally the same element. As such, there is no intrinsic fuel or oxidizer in an HEDM.

Recent research into HEDMs has focused on nitrogen. This focus can be understood by considering bond energies for nitrogen in different configurations. The $N \equiv N$ triple bond in N_2 has a dissociation energy of 954 kJ mol^{−1}, while the $N = N$ double bond is 418 kJ mol^{−1}, and the $N - N$ single bond is 160 kJ mol^{−1}. In other words, the triple bond energy is greater than 3/2 times the double bond, and greater than 3 times the single bond. Thus, the decomposition of nitrogen HEDMs into N_2 gas can release large amounts of energy on the order of several hundred kilojoules per mol of nitrogen atoms, which is slightly less than the energy released per carbon atom from the combustion of common fuels. A hard upper limit for energy that can be stored and released by a nitrogen HEDM can be estimated as 477 kJ per mol of nitrogen atoms, corresponding to a gravimetric energy density of 34 MJ kg^{−1}. The energy density of state-of-the-art

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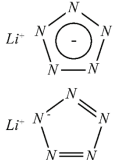
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nitrogen HEDMs is in the range from 1 to 10 MJ kg⁻¹,² which is slightly less than fossil fuels, which are in the range from 10 to 50 MJ kg⁻¹ if the mass of the oxidizer is omitted. The advantage of nitrogen HEDMs is that they can release energy very quickly, making them attractive for application as explosives and propellants. Another feature of polynitrogen compounds is that they can decompose cleanly into nitrogen gas and do not have intrinsic CO₂ emission. The performance characteristics of nitrogen HEDMs are reported to already be competitive with the conventional explosives TNT, RDX, and HMX.² A major challenge is synthesis of next-generation polynitrogen compounds. The state-of-the-art class of polynitrogen compounds is pentazoles, which consist of a cyclic 5-nitrogen anion ring together with a complementary positively charged species, such as lithium (Table 1). There are only two known routes for

Table 1. Structure and Enthalpy of Formation for Elemental Nitrogen, Lithium Azide, and Lithium Pentazolate

Name	Formula	Structure	$\Delta H_f^{298} / \text{kJ mol}^{-1}$
Elemental nitrogen	N ₂	$N \equiv N$	0
Lithium azide	LiN ₃	$Li^+ (N-N \equiv N)^-$ $Li^+ (N = N = N)^-$	+10.9
Lithium pentazolate	LiN ₅		+244

synthesizing pentazoles, and each has drawbacks.^{1,2} New synthesis methods that are safe, effective, and scalable could advance the field significantly.

Nonequilibrium plasmas are partially ionized gases that operate very far from local equilibrium. The minimum description of the reaction medium is gaseous molecules and ions that can have a temperature near ambient, intermixed with extremely high temperature electrons that are selectively heated by a high frequency field oscillating in the range 10 kHz to 10 GHz depending on the purpose of the apparatus. The electrons typically have a nonequilibrium energy distribution function with a temperature in the range $k_B T_e = 1.0$ to 10 eV, depending on the conditions used to generate the plasma. A portion of the population of these hot electrons have sufficient kinetic energy to produce through collisional processes highly excited and reactive molecular gases. For example, the first electronically excited state of N₂ ($A_3\Sigma_u^+$), which has a radiative lifetime of seconds and an energy of 6.2 eV (598 kJ mol⁻¹), is believed to be a chemical reservoir of reactivity in nonequilibrium plasma.¹⁰ Vibrational excitation to high quantum numbers is also possible through engineering of the plasma generation method,¹¹ and molecules can even be dissociated into their atomic constituents, such as atomic N.¹² All of this can be accomplished while maintaining a low background temperature, which is critical because decomposition temperatures for known pentazolate compounds are typically 100 °C or less at ambient pressure. This unique reaction environment in nonequilibrium plasmas has been used to activate relatively inert molecules¹³ to perform chemistry at low temperature, for example N₂,^{14–17} CO₂,^{17–20}

and CH₄^{17,21–23} can all be made to react at relatively low background temperature and pressures from vacuum to near ambient.

Since the nonthermal plasma reaction medium is not constrained by local equilibrium,^{24,25} product mixtures can be synthesized that are not expected at any temperature for the reactor pressure.²⁵ For long reaction times, the product mixtures are usually, but perhaps not always,²⁶ shifted in the endothermic direction relative to the equilibrium composition.^{18,25,27} In other words, the preponderance of empirical experimental evidence suggests nonequilibrium plasma is most effective at promoting *endothermic* overall reactions *past the equilibrium composition* to obtain product distributions that are not expected for any temperature at the system pressure, which again is typically from vacuum to near ambient.

This capability of producing products that are not the thermodynamic equilibrium configuration for any temperature at the system pressure is critical for the synthesis of pentazoles from N₂ gas near ambient pressure. Nonequilibrium plasma has a well-documented capability of synthesizing, under vacuum conditions, phases of materials that are equilibrium configurations only at high pressure (>10⁴ bar). The most notable canonical example is probably the synthesis of diamond phase carbon under vacuum using plasma-chemical vapor deposition.²⁸ This result is impressive since diamond does not become the equilibrium phase of solid carbon until pressures greater than approximately 4×10^4 bar. More recent work has focused on synthesis of dense phases of e.g. Ga₂O₃ by controlling the interaction of the material with the plasma during synthesis.^{29,30} Since plasmas can produce a chemically reactive environment at low temperature involving the excitation of N₂ gas and are capable of synthesizing, under vacuum, phases that are usually only observed at high pressure, plasmas are therefore attractive for the synthesis of polynitrogen HEDMs. Indeed, there have already been some early movers in the area, and promising results have been obtained.^{31–36} The field remains very much open, and breakthroughs surely await therein.

■ STRUCTURE AND STABILITY

Pentazoles can be stabilized by a variety of factors, which makes some of them metastable enough to experimentally synthesize and retain near ambient temperature and pressure.^{37–41} Aromatic molecules containing π bonds are generally more stable than their open chain analogs due to electron delocalization,⁴² which is why the focus in recent years has been on cyclic pentazoles instead of linear five nitrogen chains. To satisfy the need of each nitrogen to have three bonds, an extra electron is needed in a 5-nitrogen ring, and thus the pentazolate group must be bonded to a less electronegative species, such as hydrogen, or be present as a negative ion, for example in an ionic salt. The aromatic stabilization energy of the negative pentazolate ion has been found to be higher than pentazole,⁴² so salts are the focus here because they are expected to be more stable. Metals of the alkaline (e.g., Li, Na, K, etc.) and alkaline earth (e.g., Be, Mg, Ca, etc.) columns of the periodic table readily give up their electrons, having much lower electronegativity than nitrogen. Indeed, the addition of alkaline metals has been shown to stabilize cyclic 5- and 6-nitrogen rings.^{5,38} The incorporation of such metals to stabilize polynitrogen as stoichiometric pentazolate salts, for example Li⁺N₅³⁷ or Mg²⁺(N₅)₂⁴³ is expected to be important for new synthetic routes, such as nonequilibrium plasma synthesis for polynitrogen molecules. Metal–pentazolate salts may not have the most

attractive properties for application as explosives and propellants. However, if safe, effective, and scalable synthesis methods for metal–pentazolate salts could be developed, then wet chemical approaches such as metathesis reactions^{39–41} could be employed to exchange a metal cation for something more attractive. For examples of more attractive cations from an energetic materials perspective, see the review of Wozniak and Piercey for an overview of the properties of various pentazolate compounds.²

The purpose of polynitrogen HEDMs is to decompose and release energy. Therefore, the materials intrinsically have a positive enthalpy of formation at standard temperature and pressure, thereby ensuring an exothermic decomposition near ambient conditions. Thus, the synthesis of polynitrogen salts from the elements is an endothermic reaction. Indeed, the magnitude of the enthalpy of formation is considered a performance metric of polynitrogen materials, as well as the activation barrier to decomposition, which influences the ambient thermal metastability and decomposition temperature. The incorporation of more nitrogen into the material can increase the enthalpy of formation on a per-nitrogen basis. For example, lithium azide (LiN_3) has a relatively modest enthalpy of formation 10.9 kJ mol^{-1} ,⁴⁴ corresponding to 3.6 kJ per mol of nitrogen atoms. Lithium pentazolate (LiN_5), on the other hand, has been reported to have an enthalpy of formation 244 kJ mol^{-1} ,⁴¹ corresponding to a much higher 48.8 kJ per mol of nitrogen atoms. A similar effect can be observed with silver as the cation, where the azide has an enthalpy of formation 102 kJ mol^{-1} of nitrogen,⁴⁴ while the pentazolate has been reported to have a higher value of 165 kJ mol^{-1} of nitrogen.³⁹ Thus, candidate synthesis processes for the preparation of pentazolates from azides and N_2 gas near ambient pressure must be capable of promoting endothermic transformations on the order of 100 kJ mol^{-1} at temperatures less than 100°C , which is the typical decomposition temperature of known pentazolates that are metastable under ambient conditions.

Under conditions controlled by local thermodynamic equilibrium, the synthesis of known pentazolate compounds from elemental N_2 is only possible at high pressure ($>10^5 \text{ bar}$), 10 to 100 times higher than the pressures required to synthesize diamond phase carbon. Computational chemistry has played a prominent role in the development of polynitrogen HEDMs,² since the materials are very difficult to synthesize and can be violently unstable under ambient conditions. Plotted in Figure 1 are examples of convex hulls for the Mg–N system at pressures of 1 and $2 \times 10^5 \text{ bar}$. It can be seen that for 1 bar total pressure, the only compound that forms at equilibrium is Mg_3N_2 , which is present as a physical mixture with either Mg or N_2 depending on whether the system is N-rich or not. However, at a high pressure of $2 \times 10^5 \text{ bar}$, which can be realized experimentally in diamond anvil cells, there are a variety of magnesium–nitrogen compounds on the convex hull, including the pentazolate salt $\text{Mg}(\text{N}_5)_2$. Similar computational studies suggested the existence of thermodynamically stable LiN_5 , NaN_5 , and CsN_5 phases at high pressure, and indeed such materials have been experimentally synthesized. For example, LiN_5 was synthesized by the direct reaction of lithium metal with elemental nitrogen,^{37,45} while NaN_5 and CsN_5 were synthesized from their respective azides (NaN_3 and CsN_3) with elemental nitrogen,^{46,47} in all cases using diamond anvil cells at pressures in the range from 10^5 to 10^6 bar . In the case of LiN_5 , the pentazolate material was stable enough to recover after releasing the pressure to 1 bar.³⁷ Since the synthesis of a pentazolate from

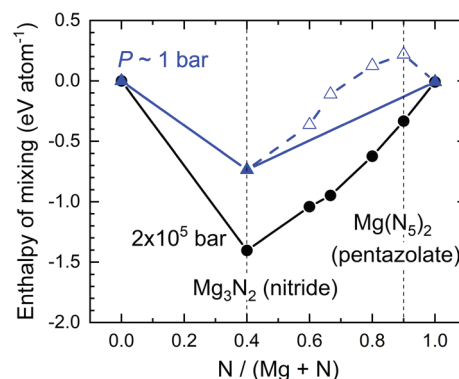


Figure 1. Convex hull of the N–Mg system at different pressures reproduced from the data in Xia et al.⁴³ At ambient pressure (blue), magnesium pentazolate is not on the convex hull, and therefore is unfavorable to synthesize from elemental N_2 under the control of thermodynamic equilibrium. At an elevated pressure of $2 \times 10^5 \text{ bar}$ (black), magnesium pentazolate is on the convex hull and is therefore expected to be a favorable product of synthesis from elemental N_2 .

nitrogen gas under vacuum, for example using nonequilibrium plasma, is expected to be difficult, starting from the respective metal azide may have a higher probability of success than starting from an elemental metal. For example, the reaction $\text{NaN}_3 + \text{N}_2 \rightarrow \text{NaN}_5$ ($\Delta H_R = 170 \text{ kJ mol}^{-1}$) may be feasible using electronically and/or vibrationally excited nitrogen gas activated from a population of hot electrons with a temperature of 1 to 10 eV. There is, of course, a question about whether NaN_5 is metastable at ambient pressure,⁴⁶ so it may be more beneficial to focus initially on a material that has been observed to be metastable at ambient temperature and pressure, such as LiN_5 , KN_5 , or AgN_5 .^{37,39,40}

MATERIAL CHARACTERIZATION

A consensus appears to be emerging on how to fingerprint metal pentazolate compounds using relatively standard characterization methods. *Caution!* pentazolate compounds are potentially air-sensitive and explosive. Characterization must be done with consideration for air exposure, and exclusion of sources of heat and ignition. Only small amounts of materials should be handled while avoiding scratching or scraping the material, and manipulations should be carried out in a hood behind a safety shield.⁴¹ Experimentalists should wear Kevlar gloves, wrist protectors (e.g., gauntlets), face shield, ear protection, and a thick leather coat.

Vibrational spectroscopy of the pentazolate ion is one of the more common methods of characterization, especially for materials synthesized by the high-pressure diamond anvil method. It exhibits a pronounced *ambient pressure* Raman scattering peak at approximately 1200 cm^{-1} , and a weaker peak at 1120 cm^{-1} .^{37,41,46,48,49} See Figure 2a for an example of an ambient pressure Raman spectrum from the work of Laniel et al. on the synthesis of LiN_5 at high pressure,³⁷ and from the work of Sun et al. on the synthesis of AgN_5 by the wet chemical route.³⁹ These peaks have been attributed to the antisymmetric and symmetric breathing modes ($\sim 1200 \text{ cm}^{-1}$) and antisymmetric breathing and deformation stretching mode ($\sim 1120 \text{ cm}^{-1}$) of the pentazolate ion.⁴⁷ Raman peaks have higher frequency at higher pressures of diamond anvil cells, and thus shifted peak positions are observed when comparing *in situ* diamond anvil data to ambient pressure data.³⁷ Laniel et al. note that at low pressure, LiN_5 becomes heat sensitive, and so low laser power

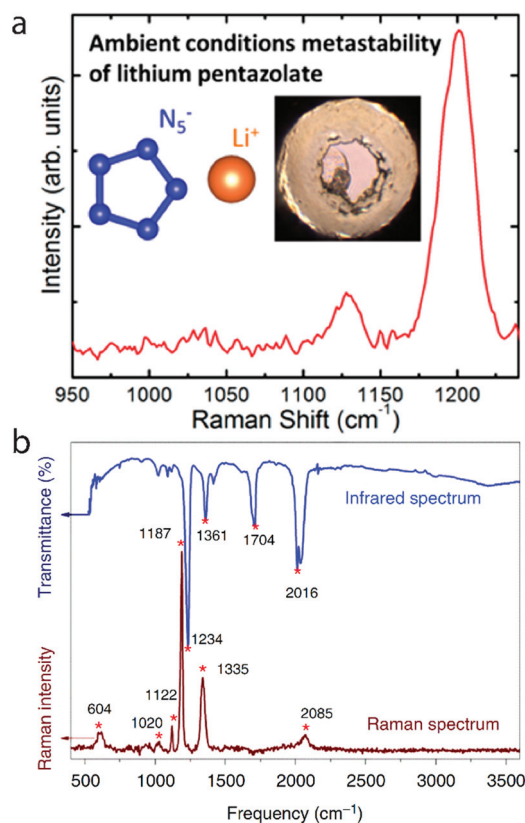


Figure 2. Vibrational spectra of the pentazolate ion in (a) LiN₅ and (b) AgN₅. Panel a was reproduced with permission from Laniel et al.³⁷ Copyright 2018 American Chemical Society. Panel b was reproduced with permission from Sun et al.³⁹ Copyright 2018 Springer Nature.

densities (a few milliwatts in their work, 648 nm laser wavelength) and commensurately long integration times (>30 s in their work) are required.³⁷ In infrared (IR) absorption, a strong *cyclo*-N₅⁻ peak has been noted in the range approximately 1210 to 1230 cm⁻¹ in a variety of compounds.^{38–41,48,49} This IR absorption peak at approximately 1200 cm⁻¹ has been emphasized in recent studies for fingerprinting purposes. See, for example, the IR absorption spectrum of AgN₅ from the work of Sun et al.³⁹ in Figure 2b.

X-ray diffraction (XRD) has been used for crystal structure determination in some metal pentazolate compounds. See, for example, sodium pentazolate,⁴⁶ cesium pentazolate,⁴⁷ and various reports of lithium pentazolate,^{37,41,50} which appears to be a promising material that exhibits metastability at ambient temperature and pressure.^{37,41} Each of these alkaline metal pentazolates exhibits a different crystal structure and lattice parameters, LiN₅ displaying monoclinic *P2* symmetry (Figure 3),^{37,45,50} NaN₅ crystallizing in the orthorhombic *Pmmn*2₁ space group,⁴⁶ and CsN₅ having a triclinic structure.⁴⁷ Furthermore, there are various compounds that can form with lesser amounts of nitrogen ranging from the alkaline nitrides (M₃N) to the alkaline pentazolates (MN₅), and mixed samples have powder diffraction spectra that can be complicated since the patterns overlap.⁴⁵ This complication renders powder XRD less useful when compared to vibrational spectroscopy and mass spectroscopy as routine characterization methods, because diffraction is difficult to use for unique positive evidence of the presence of N₅⁻ anions in the sample.

Mass spectroscopy (MS) has been successfully used by several research groups to positively identify the pentazolate ion,^{41,49,51} which has a mass-to-charge ratio of 70 AMU for the terrestrial isotopic abundance of nitrogen. These experiments involve dissolving the pentazolate salt, for example in water or methanol. The pentazolate ring is fragile, however, and therefore soft ionization methods must be used. Electron impact ionization will dissociate the ring. Electrospray ionization operating in negative ion mode has been demonstrated to preserve the parent pentazolate ion with the formula mass-to-charge ratio in the aforementioned studies. Isotopic labeling of nitrogen atoms in the pentazolate ring with N¹⁵ produced the expected shift in the mass spectrum.^{49,51} Furthermore, MS–MS techniques, whereby the parent 70 AMU ion is fragmented after classification, and those fragments are sent into a second mass spectrometer, showed that the 70 AMU peak produced fragments with 42 AMU (azide).^{49,51} Taken together with measurement of molecular nitrogen at 28 AMU upon thermal decomposition,⁴¹ a strong case can be made for pentazolate in the sample. Together with vibrational spectroscopy, MS can provide clear positive evidence of the pentazolate anion in a sample.

The currently imagined purpose of pentazolate compounds is to decompose rapidly on command and release energy. Thus,

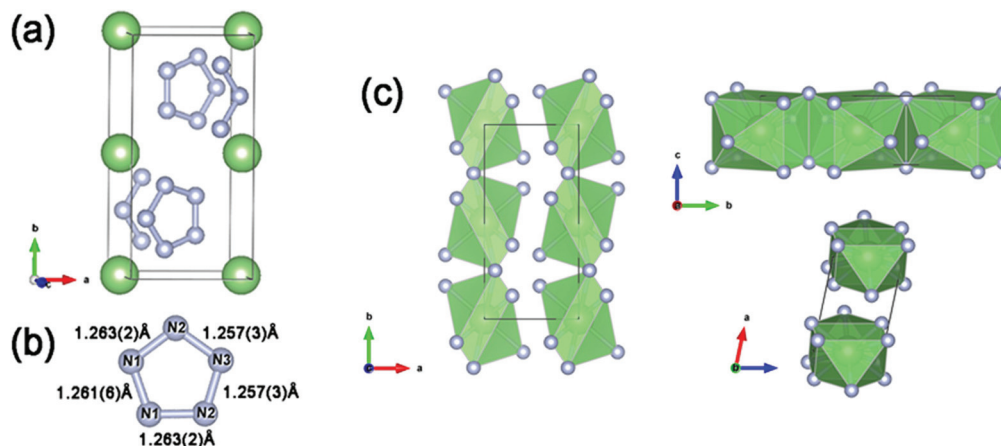


Figure 3. Crystallographic and atomic structure of LiN₅ reproduced with permission from Zhou et al.⁵⁰ Copyright 2020 American Chemical Society. (a) Unit cell of *P2*₁/*m*-LiN₅. (b) Isolated planar N₅⁻ anion in the *P2*₁/*m* structure. (c) Coordination polyhedron crystal along the *a*, *b*, and *c* axes of *P2*₁/*m*-LiN₅.

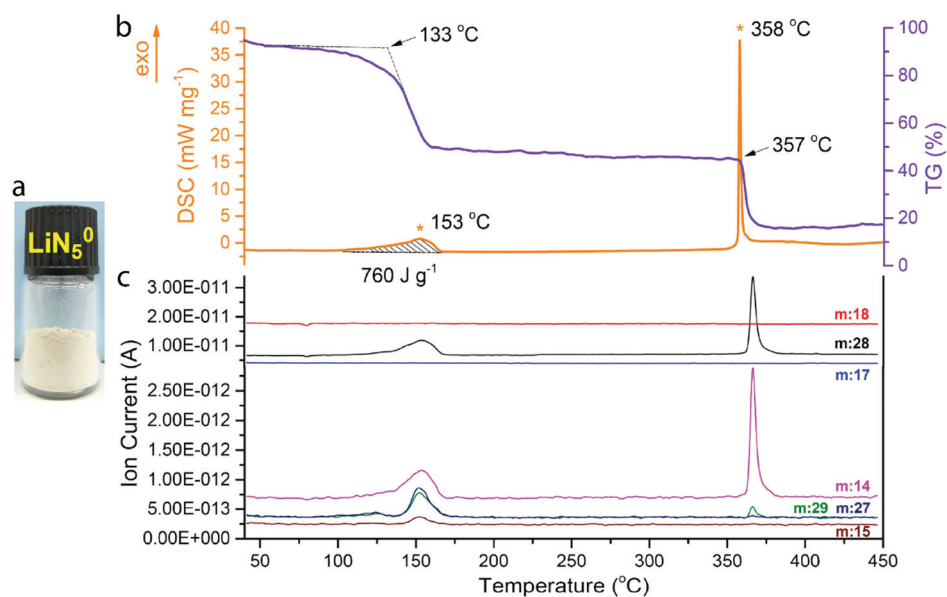


Figure 4. Decomposition characteristics of LiN_5 reproduced with permission from Xu et al.⁴¹ Copyright 2022 Elsevier. (a) Digital photograph of fresh lithium pentazolate powder. (b) Thermogravimetric (blue) and differential scanning calorimetry (orange) scans at 5 °C per minute. (c) Composition of gas emitted from sample as measured by mass spectrometry. The notation $m:x$ means the current measured from an ion with mass-to-charge ratio x .

characterization of the decomposition process, including the temperature at which various stages of the reaction occur, the energy released, and the products of the reaction, are of paramount importance to measure. These characteristics are typically measured by differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and temperature-programmed desorption (TPD). DSC, TGA, and TPD measure respectively the heat released, weight of the sample, and off-gas products as a function of temperature during a ramp. Typical temperature ramp rates used for the analysis of pentazolate salts are in the range from 5 to 10 °C per minute. Examples of DSC, TGA, and TPD data are provided in Figure 4 from the work of Xu et al. on LiN_5 synthesized by a wet chemical route using a metathesis reaction and an AgN_5 intermediate.⁴¹ The compound LiN_5 decomposes in two stages. The first stage is $\text{LiN}_5 \rightarrow \text{LiN}_3 + \text{N}_2$, which occurs at approximately 133 °C. The produced lithium azide then decomposes in a second stage at a temperature of approximately 360 °C. From this data, it can be concluded that the decomposition temperature of lithium pentazolate is approximately 133 °C. This temperature is higher than other known pentazolate salts, which all have approximately 100 °C decomposition temperature,² but still slightly less than conventional explosives such as HMX, CL-20, and ONC, which are in the range from 200 to 300 °C. Other remarkable detonation properties of LiN_5 were reported by the authors, and the interested reader can find the conclusions therein.⁴¹

■ SYNTHESIS

There are two known methods to synthesize pentazolate rings. The most common method is a wet chemical method involving the synthesis of an aromatic carbon ring with a pentazole group attached to it by a C–N bond. This method has been reviewed in detail elsewhere.^{1,2} The challenge with the wet chemical approach is cleaving the C–N bond to release the nitrogen ring from the aryl ring without destroying the nitrogen ring.³⁸ Some approaches to overcome this challenge have been developed.^{48,49} Nevertheless, the wet chemical method is the

only method that has demonstrated synthesis of significant quantities of material, see for example the Supporting Information of Xu et al. 2022 for reasonably large amounts of LiN_5 (Figure 5a).⁴¹ The second method involves reacting an azide precursor (e.g., LiN_3) or a metal precursor (e.g., Li) with elemental nitrogen N_2 to make the corresponding metal pentazolate. These reactions proceed toward local thermodynamic equilibrium only at high pressures, for example 6×10^5 bar.⁵² As such, they are typically carried out in diamond anvil cells, which have obvious limitations when it comes to scalability. Thus, new synthesis methods that are safe, effective, and scalable would be advantageous and could lead to significant breakthroughs in science and technology simply by making the material more available.

The proposal is to synthesize metal pentazolates by reacting the corresponding azide with N_2 gas that has been activated by a nonequilibrium plasma, under vacuum or near ambient pressure. For example, reaction of $\text{LiN}_3 + \text{N}_2^* \rightarrow \text{LiN}_5$ where the asterisk denotes that N_2 has been activated by a plasma. One specific example of N_2^* could be the well-known first electronic excited state $\text{A}_3\Sigma_u^+$ that has 6.2 eV (598 kJ mol⁻¹) of energy above the ground state and a long radiative lifetime,¹⁰ but there are probably others as well. This reaction to synthesize lithium pentazolate involves an enthalpy change of approximately 233 kJ mol⁻¹ (Table 1), and it is also a move away from equilibrium at pressures less than or equal to ambient. Interestingly, endothermic reactions with similar enthalpy changes have been observed to occur in nonequilibrium plasmas at pressures less than ambient and low temperature where they are not favorable from the perspective of equilibrium thermodynamics. For example, at low background temperatures where CO_2 is the equilibrium speciation in the C–O system, CO_2 was observed to spontaneously decompose into $\text{CO} + \frac{1}{2}\text{O}_2$ by passing through a nonequilibrium plasma.¹⁸ The endothermic CO_2 splitting reaction involves an enthalpy change of approximately 284 kJ mol⁻¹. Similarly, the water splitting reaction $\text{H}_2\text{O} \rightarrow \text{H}_2 + \frac{1}{2}\text{O}_2$, involving an enthalpy of reaction of approximately 242 kJ mol⁻¹, can be promoted by nonequilibrium plasma at low temperature

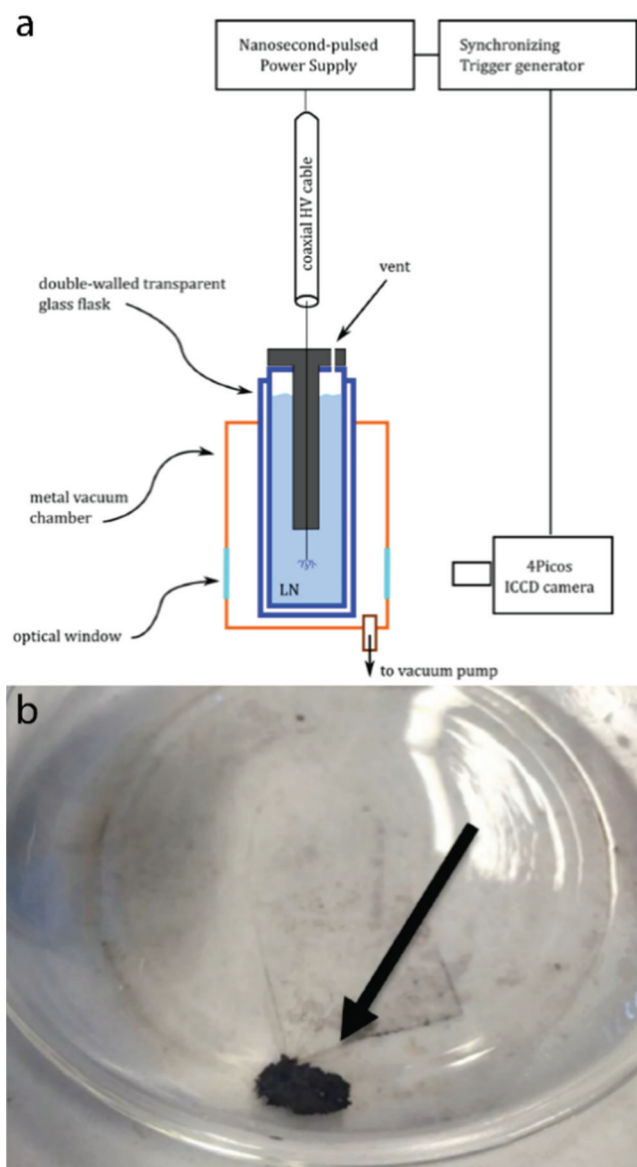


Figure 5. Plasma synthesis of polynitrogen HEDM from liquid nitrogen reproduced with permission from Dobrynin et al.³³ Copyright 2019 IOP publishing. (a) Experimental schematic used for plasma generation by repetitive nanosecond high voltage pulses in liquid nitrogen. (b) Digital photograph of solid polynitrogen material produced by 1 h of plasma treatment after evaporation of excess liquid nitrogen.

under vacuum where it is not favorable from the perspective of equilibrium thermodynamics.²⁷ Similar results have been obtained for association reactions involving N_2 chemistries, where high mole fractions of nitric oxide and hydrazine have been realized under conditions where they are unexpected in systems governed by thermodynamic equilibrium.²⁵ State-of-the-art understanding is that chemical reactions in non-equilibrium plasma are governed by a different thermodynamic principle because they take place in the nonlinear regime of irreversible thermodynamics.²⁴ While further research is clearly necessary to demonstrate that nonequilibrium plasmas are a feasible means to synthesize metal pentazolate materials, the preliminary survey of results is very promising as it clearly demonstrates: (1) plasmas can promote endothermic reactions that proceed away from the local thermodynamic equilibrium state with reaction enthalpies in the range from 200 to 300 kJ

mol^{-1} , and (2) such reactions can be made using N_2 gas as the nitrogen source, and indeed the long-lived first electronically excited state $A_3\Sigma_u^+$ of nitrogen can deliver enough enthalpy to promote the transformation of azide to pentazolate. Therefore, a gas–solid reaction between azide and N_2^* to synthesize a metal pentazolate near ambient pressure is a reasonable hypothesis to test. It is expected to be important that the solid phase temperature not be too high, since pentazolates are known to decompose above approximately 100 °C (e.g., Figure 4). However, that stability of the pentazolate with temperature may be dependent upon the environment of the solid, and the density of activated nitrogen N_2^* therein.

The preliminary *avant garde* results on the synthesis of polynitrogen compounds using plasmas operating very far from local equilibrium are encouraging. Dobrynin et al. have published a series of papers in which they generated nanosecond pulsed plasmas in liquid nitrogen near ambient pressure.^{31–33} A dark solid product was formed from this plasma reaction (Figure 5), which exhibited some metastability at very low temperatures near the liquid nitrogen boiling point. Upon heating to ambient temperature, this material exploded leaving no residue.³³ In a follow-up work,³² the team added sodium azide to the liquid nitrogen, which settled out of the bottom of the reaction vessel, but was nevertheless modified by the plasma treatment. After treatment, the solid residue exhibited features in vibrational spectroscopy consistent with N_6 materials. The authors report a material that was metastable at ambient pressure up to temperatures of approximately –55 °C. Although the authors report that metal introduction into the liquid nitrogen by electrode erosion was possible, and indeed this metal addition may stabilize polynitrogen species (*vide supra*), the experimental results of Dobrynin et al. provide strong evidence that plasma activation of elemental nitrogen can result in the synthesis of nitrogenous HEDMs. In the most recent installment of this series of papers,³¹ the authors report an experimental measurement of 13 MJ kg^{-1} for detonation of this plasma-synthesized nitrogenous material, which is an impressively high number among polynitrogen compounds, approximately 38% of the upper limit for this class of materials based on the enthalpy of formation of atomic gaseous N.

The group at the New Jersey Institute of Technology has also published a series of papers on the synthesis of polynitrogen compounds supported and unsupported by carbon nanotubes from NaN_3 as well as electrochemically prepared N_8^- .^{34–36} Benchafia et al. reported in 2017 on the radiofrequency plasma synthesis near ambient pressure of a material, using sodium azide and nitrogen gas as precursors, which showed vibrational spectra and diffraction patterns consistent with the cubic gauche polymorph of polynitrogen.³⁵ The authors bring an important point to the fore, which is the role of a support in stabilizing polynitrogen species. Unfortunately, no detonation results were presented, and so the properties of the synthesized material for energetic applications remain unknown. In a follow-up detailed study in 2022 from the same group, Zhuang et al. reported on a similar system. They explored both carbon nanotube-supported and unsupported NaN_3 , as well as N_8^- precursors.³⁴ Vibrational spectroscopy again, combined with diffraction and density functional theory simulations, supported the claim of radio-frequency nitrogen plasma synthesis of the cubic gauche polymorph of polynitrogen at ambient pressure. TPD experimental results were presented. Somewhat surprisingly, on carbon nanotube supports, the authors report that the cubic-gauche polymorph decomposes into N_2 gas at a higher

temperature than NaN_3 . No DSC or TGA results were presented, so it is unclear how applicable this material is to energetic applications. The authors have presented some interesting electrochemical behavior of the materials.³⁴

The reported preliminary evidence suggests that there probably needs to be a condensed phase precursor involved in the synthesis of polynitrogen compounds by nonequilibrium plasma (Figure 6). This condensed phase is expected to serve

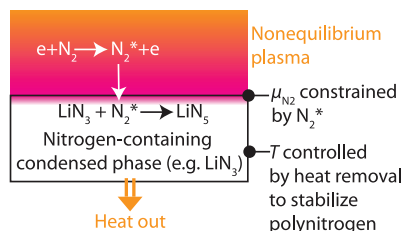


Figure 6. Schematic of a hypothetical mechanism to synthesize polynitrogen compounds by nonequilibrium nitrogen plasma. This hypothesis is untested.

two purposes: (1) it hosts the pentazolate compound, which is expected to be a condensed phase, mixed into a condensed phase, or on the surface of a condensed phase, and (2) it keeps the pentazolate temperature low to prevent thermal decomposition. Hypothetically, the plasma would act as a source of excited nitrogen N_2^* which would then be transported to an adjacent nitrogen-containing condensed phase. While the nonequilibrium plasma is not governed by local equilibrium, the adjacent nitrogen-containing condensed phase probably is, at least under most circumstances. The thought is that the N_2^* coming from the plasma has sufficient chemical potential to promote nitrogen polymerization reactions in the condensed phase. The metastable first electronically excited ($A_3\Sigma_u^+$) state of N_2 has sufficient chemical potential, but there are probably other excited states that would work as well. In other words, the idea is that the nitrogen chemical potential is constrained at the interface by N_2^* from the plasma and that the condensed phase will react to equilibrate with that constrained chemical potential of nitrogen. The task then becomes to control that equilibration such that the nitrogen-containing condensed phase reacts to transform into a desired polynitrogen compound. Figure 6 is an untested hypothesis and therefore speculative, but it is consistent with the reported experimental results on plasma-synthesis of polynitrogen compounds. In the experiments of Dobrynin et al., the adjacent condensed phase was liquid nitrogen, and in the experiments of the New Jersey Institute of Technology, the adjacent condensed phase was sodium azide.

CONCLUSIONS

In conclusion, the perspective is that polynitrogen high energy density material (HEDM) synthesis by nonequilibrium plasma is a promising and open field for research and that metal pentazolate salts are a promising near-term synthetic target. Several metal pentazolate salts have been reported to be metastable at ambient temperature and pressure, including LiN_5 , KN_5 , and AgN_5 . There are two independent experimental methods that can be used to positively identify the 5-nitrogen ion in a material, specifically vibrational spectroscopy (i.e., Raman scattering and IR absorption) and electrospray ionization-mass spectroscopy. X-ray diffraction can be used as an additional method. Some preliminary attempts to synthesize

polynitrogen HEDM by nonequilibrium plasma near ambient pressure have been successful, and there is clearly more research to be done to realize a method that is safe, effective, and scalable.

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Notes

The author declares no competing financial interest.

Biography

Dr. Elijah Thimsen is currently an associate professor at Washington University in Saint Louis. He was raised in St. Paul Minnesota and currently resides in St. Louis, Missouri. Dr. Thimsen has over 20 years of experience doing technical research, most of which was focused on the synthesis of advanced materials by gas-phase methods. He was raised as a child by two parents, one of whom was a project manager for the Electrical Power Research Institute and the other was a professional costume designer. He obtained his undergraduate degree in mechanical engineering at the University of Minnesota under the supervision of Uwe Kortshagen, and his philosophy doctorate in energy, environmental, and chemical engineering at Washington University in Saint Louis under the supervision of Pratim Biswas. Dr. Thimsen's work has been recognized by a variety of organizations, including recently by the National Science Foundation and Department of Energy early career awards.

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ABBREVIATIONS

HEDM, High Energy Density Material
DSC, Differential Scanning Calorimetry
TGA, Thermogravimetric Analysis
TPD, Temperature-Programmed Desorption

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