

Green bipropellant development – A study on the hypergolicity of imidazole thiocyanate ionic liquids with hydrogen peroxide in an automated drop test setup

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Abstract

Conventional hypergolic propellant combinations, using hydrazine and its derivatives as fuels and dinitrogen tetroxide based oxidizers, have been applied in spacecraft for attitude and roll control systems for more than 50 years. However, due to their high toxicity and carcinogenic potential, investigations into alternative green propellants are an active field in current research efforts. Promising alternative propellant candidates are combinations of hydrogen peroxide and suitable hypergolic room-temperature ionic liquids. In this work, imidazole thiocyanate ionic liquids are tested in drop tests with hydrogen peroxide. For this purpose, a newly developed automated drop test setup was designed and implemented. As a result, 1-ethyl-3-methylimidazolium thiocyanate (EMIM SCN) and 1-butyl-3-methylimidazolium thiocyanate (BMIM SCN) turned out to be hypergolic with highly concentrated hydrogen peroxide (96.1%). The ignition delay time on average is 31.7 ms for EMIM SCN

and 45 ms for BMIM SCN. Theoretical performance of the two ionic liquids was calculated with NASA CEA and compared to a conventional hypergolic propellant combination (monomethyl hydrazine / dinitrogen tetroxide). The specific impulse of the green propellants is nearly 5 % lower, but the density specific impulse is increased by 10 %. Furthermore, the ignition delay time was reduced by dissolving a catalytic additive, copper thiocyanate, in the EMIM SCN. The lowest average ignition delay time of 13.9 ms was achieved for EMIM SCN and 5 wt% of copper thiocyanate. For higher copper concentration the ignition delay time is not further reduced. The fuel with EMIM SCN and 5 wt% of copper thiocyanate and the pure EMIM SCN were further characterized by thermal and spectroscopic methods. Fluid properties like density, viscosity and surface tension were also determined in laboratory investigations.

1 Introduction

Hypergolic propellants are the first choice for large spacecraft's attitude and roll control systems. 50 years ago, hypergolic propellants were used for the Apollo spacecraft to go to the moon and back as well as for the lunar module landing and ascent into orbit [1]. Nowadays hypergolic propellants are used to return to the moon, a typical example being the European service module of the Orion spacecraft [2]. The conventional flight proven hypergolic propellants use hydrazine or its derivatives as fuel and an oxidizer based on dinitrogen tetroxide (NTO). Hydrazine and its derivatives, unsymmetrical dimethyl hydrazine (UDMH) or monomethyl hydrazine (MMH), are toxic and carcinogenic. In Europe, hydrazine was added to the candidate list of substances of very high concern as part of the REACH (registration, evaluation, authorization of chemicals) regulation [3]. As a consequence, it is possible that the use of hydrazine will be banned in Europe. Thereafter, the use of hydrazine derivatives could also be restricted. NTO is toxic, highly corrosive and has a very high vapor pressure at ambient conditions. NTO forms a highly toxic cloud if released from its containment due to leakage or spill. Due to these noxious properties of hydrazines and NTO, extensive safety precautions for handling are necessary, such as self-contained atmospheric protective ensemble (SCAPE) suits. Thus, handling of conventional hypergolic propellants imposes high additional costs during production, storage, transportation and fueling. Alternative green propellants are developed to overcome the adverse effects of highly volatile and toxic conventional propellants. With green propellants, safety handling requirements can possibly be less extensive which offers a high cost reducing potential.

1.1 Alternative green bipropellants

Commercially available high performing liquid oxidizers for green hypergolic propellant combinations are limited. Suitable oxidizers are highly concentrated hydrogen peroxide, red, or white fuming nitric

acid, and NTO or mixtures with different oxides of nitrogen (MON). From this list, hydrogen peroxide (H_2O_2) is the “greenest” option with the least toxicity and a very low vapor pressure. Highly concentrated hydrogen peroxide, also referred to as high test peroxide or HTP, was flight proven in the 1960s as part of the Mercury program. Hydrogen peroxide is still in use today as a monopropellant in the reaction control system of the Soyuz descent module [4]. The first hypergolic fuels with hydrogen peroxide were developed during the Second World War in Germany [5].

A renewed interest in hypergolic fuels with hydrogen peroxide resurfaced in the last three decades, starting with the development of non-toxic hypergolic miscible fuels (NHMF) in the mid-1990s in the USA [6]. Of late, different fuel blends were investigated because pure hypergolic substances with H_2O_2 are scarce. The fuel blends consist of liquid organic compounds and a dissolved additive. These additives either take effect on the decomposition of hydrogen peroxide or directly reduce the hydrogen peroxide. Such developments have recently been conducted by research groups at the Institute of Aviation in Poland [7-9] and the Korea Advanced Institute of Science and Technology in South Korea [10-13].

Another promising group of potential fuels are room-temperature ionic liquids (RTILs), which have a negligible vapor pressure at ambient conditions. Through a combination of different cation and anions, the physical properties can be directly influenced. By this approach, fuels can be produced that are hypergolic with HTP, boast low viscosities, and have a high energy content. In 2008, a research group at the Air Force Research Lab at Edwards Air Force Base reported the first hypergolic ionic liquid (HIL) [14, 15]. Many HILs have been developed in the last 12 years [16-18]. Most of these ionic liquids are hypergolic with white fuming nitric acid (WFNA). Hypergolicity of ionic liquids is mostly driven by the anion [16]. The structure of the large organic cation influences the HIL's physical properties such as viscosity, density, ignition delay time and heat of formation [19].

Only very few investigations were conducted with the aim to identify pure hypergolic ionic liquids with hydrogen peroxide. In 2011, a hypergolic ionic liquid with an $\text{Al}(\text{BH}_4)_4^-$ anion was found to be hypergolic with hydrogen peroxide [20]. The ignition delay time is less than 30 ms when reacting with hydrogen peroxide at a concentration of more than 90%.

Different blends of ionic liquids have been investigated by several groups. Schneider et al. patented mixtures of ionic liquids as hypergolic fuels [21]. The fuel consists of two ionic liquids: the first is a metal containing ionic liquid which serves as catalyst, whereas the second ionic liquid acts as the fuel. A group at Tel Aviv University in Israel also worked with ionic liquids blends, where one component has a catalytic metallic cation based on iodide and iodocuprate [22, 23]. Kim et al. investigated mixtures of 2-hydroxyethylhydrazine and ionic liquids with different anions. Azide (N_3^-), cyanide (CN^-), iodide (I^-

), and tetrachloroaluminate (AlCl_4^-) reached ignition delay times between 8 – 33 ms [24]. Weiser et al. investigated 1-allyl-3-methylimidazolium dicyanamide [25]. This ionic liquid is hypergolic with WFNA but did not show reactivity with hydrogen peroxide. To introduce hypergolic behavior, a copper salt was dissolved in the fuel and ignition delay times down to 9 ms were observed. In investigations by Bhosale et al., the most promising pure ionic liquid in terms of ignition delay time is EMIM BH_4 at 18 ms, but it is not liquid at room temperature [26]. Other ionic liquids with the BH_3CN^- anion showed ignition delays with 95 % hydrogen peroxide on the order of one second [26]. Bhosale et al. were able to reduce the ignition delay times of EMIM BH_3CN with different additives [27]. Various additives were investigated, but catalytic additives such as transition metal salts copper (II) chloride, manganese (II) acetate, cobalt (II) acetate, and the reactive additive sodium borohydride, showed limited solubility and limited reduction of the ignition delay. The most promising additive was a salt with a copper iodine anion that showed good solubility and ignition delay times down to 13 ms.

To the best of our knowledge, only one pure room temperature ionic liquid has been found which is hypergolic with hydrogen peroxide within 30 ms [20]. In many other investigations additives based on transition metals were needed to introduce fast hypergolic behavior [21-25, 27]. But high amount of metal additives can have adverse effects such as reduction of the specific impulse (I_{sp}) due to the higher molecular mass. Metallic components can also form oxides, resulting in solid particles in the plume. This could have the unintended side-effect of damaging surfaces such as solar panels if the plume is directed towards them.

1.2 Recent developments

A research campaign at the Institute of Space Propulsion at the DLR Lampoldshausen is dedicated to the development of different hypergolic fuels with hydrogen peroxide, focusing on fuels based on room temperature ionic liquids [28-31]. The requirements for ionic liquid fuel candidates were defined in [28]. The driving factor for the first investigations was the commercial availability of the ionic liquid because relevant data has already been published. Relevant data includes physical properties such as density, viscosity, melting point and enthalpy of formation. Other properties of interest regarding safety and easy handling are impact, friction or electronic discharge sensitivity, and toxicity. For long term storability, fluid properties like thermal stability, hygroscopicity and material compatibility need to be assessed. Unfortunately, the required data is not available for many ionic liquids. Therefore, they need to be investigated in later activities after potential fuel candidates have been identified. As a result of the theoretical screening, investigations at the DLR studied the ionic liquid, 1-butyl-3-methylimidazolium acetate, which proved not to be hypergolic with hydrogen peroxide [28]. With the introduction of a copper or manganese salt, hypergolic behavior in drop tests was observed. Mixing of oxidizer and fuel was very poor, resulting in ignition delay times on the order of a hundred milliseconds.

Therefore, a solvent was introduced into catalytically promoted ionic liquid fuels [29]. The mixing was improved and ignition delay times on the order of 30 ms were determined in drop tests. After the initial drop test screening at the DLR, potential hypergolic fuel candidates can be tested under a flowing condition in a hypergolic injector test setup, (HIT) described in further detail in ref. [32].

In the present work, the very promising results obtained from the drop tests conducted with imidazole thiocyanate ionic liquids with 96.1% hydrogen peroxide are described. The fuels have been tested pure and with the addition of a catalytic promoter. The most relevant physical and thermal properties of the fuels with the shortest hypergolic ignition delay have been characterized.

2 Material and methods

2.1 Materials: rationale behind the selection of ionic liquids

A preliminary theoretical screening of commercially available ionic liquids was conducted and different ionic liquid based fuels were investigated in drop tests [29, 28]. For the present study, a novel group of ionic liquids based on the thiocyanate anion was chosen for further investigation. 1-ethyl-3-methylimidazolium thiocyanate (EMIM SCN) and 1-butyl-3-methylimidazolium thiocyanate (BMIM SCN) ionic liquids are commercially available and a lot of property data has been published on their characteristics. The thiocyanate ionic liquids offer low melting points ($< 0^{\circ}\text{C}$), moderate viscosities (< 50 mPa s), and in the case of EMIM SCN, a positive enthalpy of formation (see Table 1). Furthermore, it has been reported that EMIM SCN is mixable with water [33] which makes it very likely miscible with hydrogen peroxide. According to literature [34] hydrogen peroxide shows the same solvent relationships with other liquids as pure water shows with those liquids. This is beneficial for efficient mixing and fast hypergolic ignition. Zarca et al. investigated properties of EMIM SCN with dissolved copper (I) thiocyanate (Cu SCN) [35]: if ionic liquid and a salt share the same anion it is possible to dissolve a high amount of the salt. The dissolved metal salt offers the possibility to promote the reaction with the hydrogen peroxide.

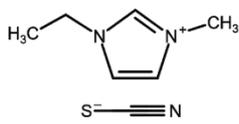
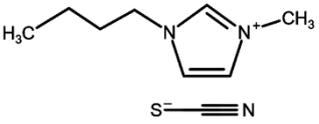
Toxicity of ionic liquids needs to be considered for use as a green fuel. The vapor pressure of ionic liquids at ambient conditions is negligible. Therefore, contamination of air with toxic vapors from the fuel can be disregarded. This is a substantial advantage compared to the conventional hypergolic propellants based on NTO and hydrazines. EMIM SCN has an ecotoxicity (EC_{50} , 15 min) towards the aquatic organisms *Vibrio fischeri* of 6310 mg/l and BMIM SCN has 513 mg/l [36]. The EC_{50} concentration of EMIM SCN is classified as “harmless” and “practically harmless” of BMIM SCN according to the classification by Passino and Smith [37].

Sun et al. investigated hypergolic ignition of 1-allyl-3-methylimidazolium thiocyanate with WFNA [38]. In their investigation, the thiocyanate ionic liquid showed an ignition delay time of 200 ms. As far as the authors are aware, thiocyanate ionic liquids have not been evaluated on hypergolic behavior with hydrogen peroxide yet.

2.2 Materials: fuels and oxidizer

1-ethyl-3-methylimidazolium thiocyanate and 1-butyl-3-methylimidazolium thiocyanate were purchased from *Iolitec*, Germany. The purity of the ionic liquid is specified by the producer to be higher than 98%. The properties of the two ionic liquids are shown in Table 1. Hydrogen peroxide, *Propulse*[®] 980, was purchased from *EVONIK* and stored for about two and a half years before the presented experiments in 1l aluminum bottles provided by the manufacturer. During the first year the hydrogen peroxide was stored at ambient conditions and the rest of the time at 5°C. The actual concentration of hydrogen peroxide was determined directly before testing by measuring the density and using the table from [39] to correlate the measurement to the concentration. The value of the concentration was 96.1 wt%. All chemicals were used as purchased and tested without any further purification.

Table 1 Properties of commercial thiocyanate ionic liquid: melting point (T_m), density at 25°C (ρ), viscosity at 25°C (η), enthalpy of formation ($\Delta_f H^0$)

| | | T_m [°C] | ρ [g/cm ³] | η [mPa s] | $\Delta_f H^0$ [kJ/mol] |
|---|---|---------------|--------------------------------|-------------------|----------------------------|
| 1-ethyl-3-methylimidazolium thiocyanate |  | -6 [40] | 1.11 [33] | 22.7 [33] | 52.8 [41] |
| 1-butyl-3-methylimidazolium thiocyanate |  | -29 [42] | 1.07 [43] | 35.8 [43] | -5 [44] |

2.3 Materials: catalysts

The catalytically promoted fuels consist of EMIM SCN and the catalytic additive copper (I) thiocyanate, (>96%, *Alfa Aesar*) in different weight concentrations (0.5 wt% up to 10 wt%). The amounts of fuel and additive were weighted corresponding to the desired concentration. The additive was dissolved in the ionic liquid fuel by stirring it at 70° C for 2 hours. The temperature was increased to shorten the dissolution process, especially for the fuels with higher additive content. The additive was completely dissolved in all cases. After cooling to room temperature no precipitation of solid material for any

concentration was observed. The catalytically promoted fuels remained stable after mixing for several months stored at ambient conditions. The fuels are shown in Figure 1.

2.4 Methods: automated drop test setup

A simple method to evaluate reactivity of the components of a propellant combination is through a drop test. One component (A) of a propellant is dropped onto the second component (B). This is recorded with a high-speed camera. The ignition delay time can be determined by analyzing the high-speed recordings. For this investigation, a newly built automated hypergolic drop test setup was utilized. The setup consists of a closed reaction chamber, a propellant supply system, controlling, and measuring computer. The chamber has a quadratic cross section with inner dimension of 140 mm x 140 mm and a height of 216 mm. The walls are made from the aluminum alloy EN AW 6060. The chamber has a removable side panel to allow accessibility. The chamber can be evacuated or filled with inert gas. Furthermore, the chamber is optically accessible from three sides, allowing recording from different vantage points with the high-speed camera. With this apparatus, flame emission and absorption spectroscopy are also possible. The propellant supply system consists of a self-made syringe pump. Two plastic medical syringes are connected to cannulas. The syringes can be filled with the two components of the propellant. The plungers of the syringes are connected to linear motors. By moving the plunger of the syringe, the contents can be dropped into the reaction chamber. Inside the chamber, there is a watch glass that contains a pool of component B of the propellant. One of the cannulas is placed centrally above of the watch glass. The “dropped” component A is released from the central cannula. The second cannula is located at some distance from the central cannula above the watch glass to provide the component B of the propellant. Eight drops of the component B are dropped first and gather in the middle of the watch glass because of the concave surface and form a pool. Then the high-speed camera is started and the component A is dropped from the central cannula. The scheme of the entire setup as well as the inside of the reaction chamber is shown in Figure 2.

After a drop test it is possible to flush the watch glass with water as a cleaning liquid. The watch glass can then be turned using a motor. A water spray suppresses ongoing hypergolic reactions and cleans the watch glass.

The chamber is placed inside a fume hood for safety reasons. The tests presented were conducted with a fuel pool and a drop of oxidizer at ambient pressure, ambient temperature, exposed to air. The average fuel amount in the watch glass was $115 \mu\text{l} \pm 15.2 \mu\text{l}$, the oxidizer drops had an average volume of $14 \pm 2.3 \mu\text{l}$ and the drop height was 61 mm. The amount of fuel and oxidizer were approximated by determining the diameter of the drops by means of the high-speed recordings: the drop was assumed to be spherical, the diameter of the sphere was determined in terms of pixels and the pixels were related to a reference length. For the determination of the reference length as well as the diameter an

uncertainty of 3 pixels was assumed. The overall uncertainty of the drops is calculated according to Gaussian error propagation. Amounts of fuel, oxidizer and drop height were kept constant for all presented tests. For the determination of the ignition delay, high speed imaging was used. In an initial test campaign of hypergolicity tests with pure BMIM SCN and EMIM SCN a *Photron fastcam SA1.1* monochrome high-speed camera was used. In a second test campaign where EMIM SCN and the influence of the catalytic additive was investigated, a *Photron fastcam SA-X2* color high-speed camera were used. The Photron fastcam SA1.1 has a maximum frame rate of 675k frames per second (fps) and a pixel size of 20 μ m x 20 μ m. During the drop tests the resolution was set to 384 x 888 pixel at a frame rate of 2000 fps. The Photron fastcam SA-X2 type 480 has a maximum frame rate of 480k fps and a pixel size of 20 μ m x 20 μ m. During the drop tests the resolution was set to 768 x 1016 pixel at a frame rate of 3600 fps. The sensitivity of the sensor ranges from 400 to 700 nm.

2.5 Methods: characterization of physical and thermal properties of fuels

Density measurements were conducted with a density meter Easy D40 by *Mettler-Toledo* at ambient conditions. The measurement uncertainty is ± 0.0005 g/cm³. Determination of fluid viscosity was conducted using a class II Ubbelohde viscosimeter. Surface tension measurements were performed with a *Krüss EasyDyne* tensiometer using the Wilhelmy plate method. All measurements were performed three times and the average values are used. Thermal analysis (TG/DSC) was conducted in order to compare the behavior of different ionic liquid fuels at high temperatures. A *Netzsch STA 449 F3 Jupiter*[®] thermal analyzer was used. The tests were conducted with fuel samples in closed aluminum crucibles under a nitrogen gas atmosphere at a heating rate of 10°C per minute. The ionic structure of the pure ionic liquid and the catalytically promoted ionic liquid were compared using ATR- FTIR spectra. They were recorded with a *Shimadzu IRAFFINITY-1S* spectrometer.

3 Results and Discussion

3.1 Theoretical performance evaluation

The specific impulse and the density specific impulse are important parameters which allow for comparison of the different propellant performances. The specific Impulse (I_{sp}) is defined as the ratio of thrust (F) to overall mass flow (\dot{m}) and gravitational constant (g_c):

$$I_{sp} = \frac{F}{g_c \times \dot{m}} \quad (1)$$

I_{sp} calculations were conducted in order to estimate the propulsive performance with *Chemical Equilibrium with Applications* (CEA), a thermodynamic code developed by NASA [45]. The calculations assume frozen supersonic expansion. As a reference case a 400 N thruster from *ArianeGroup* [46] was used. The expansion ratio of the nozzle $\varepsilon = A_e/A_t$ is defined as the ratio between the exit area (A_e) of the nozzle and the area at the throat (A_t) of the nozzle.

The value of ε for the mentioned thruster is 330 and the chamber pressure is 1 MPa. These values were identical to the thruster used as a reference, a 400 N thruster from *ArianeGroup* [46]. Further input parameters were heat of formation and chemical composition of the fuels, see Table 1. The oxidizer was 98 wt% hydrogen peroxide and 2 wt% water. The properties of the oxidizer components are already implemented in the CEA database. As a reference, the performance of conventional hypergolic propellant MMH/NTO was also calculated. The ratio of oxidizer to fuel (ROF) is defined as the ratio of the oxidizer mass flow ($\dot{m}_{oxidizer}$) and the fuel mass flow (\dot{m}_{fuel}).

$$ROF = \frac{\dot{m}_{oxidizer}}{\dot{m}_{fuel}} \quad (2)$$

For the density specific impulse, the average density of the propellant at the ROF corresponding to $I_{sp \max}$ was calculated as:

$$\rho_{propellant} = \frac{\rho_o \times \rho_f \times (ROF + 1)}{\rho_o + \rho_f \times ROF} \quad (3)$$

with the density of the oxidizer as ρ_o , and the density of the fuel as ρ_f .

Figure 3 shows the resulting I_{sp} values corresponding to the pressure of the nozzle exit for different ROF and three propellant combinations: the ionic liquid fuels EMIM SCN and BMIM SCN with 98 % hydrogen peroxide as oxidizer are shown and the conventional hypergolic propellant combination MMH/NTO. Table 2 lists the maximum I_{sp} , density I_{sp} , the theoretical combustion temperature at the maximum I_{sp} and the average molecular mass M of the reaction products. The maximum I_{sp} MMH/NTO is 334s at a ROF 1.8. The maximum I_{sp} of EMIM SCN is 317s at a ROF of 3.8 and the maximum I_{sp} of BMIM SCN is 319s at a ROF of 4.2. The theoretical performance of the green propellants is around 5 % lower than the conventional one. On the other hand, the density specific impulse of green propellants is 10 % higher than the conventional one. This is due to the higher density of the fuel and higher ROF. This can be an advantage in volume restricted propulsion systems, because it allows for more energy to be stored in the same volume.

A significant difference between the conventional hypergolic fluids and the proposed green propellant combinations is found in the combustion temperature at $I_{sp \max}$. The theoretical value of MMH/NTO is

300 K higher. This implies that green fuels may require a lesser amount of cooling. The difference in the maximum I_{sp} and the corresponding ROF between the two ionic liquids can be explained by the slightly different hydrocarbon side chain of the ionic liquid. The BMIM SCN has two carbon and four hydrogen atoms more than the EMIM SCN and the molecular mass is slightly lower for the BMIM SCN. On the other hand, EMIM SCN has a positive enthalpy of formation whereas BMIM SCN enthalpy of formation is negative. Higher (positive) enthalpy of formations lead to higher combustion temperatures and therefore to higher I_{sp} values. In case of the BMIM SCN the lower average molecular mass of the reaction products supersedes the drawback of the lower enthalpy of formation and results in a slightly higher maximum I_{sp} value for BMIM SCN.

Table 2 Results of I_{sp} calculation

| Propellant Combination | maximum I_{sp} [s] | ROF at $I_{sp \max}$ [-] | $\rho_{I_{sp \max}}$ [s kg/m ³] | T_c at $I_{sp \max}$ [K] | M [g/mol] |
|---|----------------------|--------------------------|---|----------------------------|-----------|
| MMH / NTO | 334 | 1.8 | 390 | 3124 | 21.3 |
| EMIM SCN / 98 % H ₂ O ₂ | 317 | 3.8 | 430 | 2828 | 23.2 |
| BMIM SCN / 98 % H ₂ O ₂ | 319 | 4.2 | 431 | 2824 | 22.9 |

3.2 Drop test

Examples of drop tests conducted with different fuels are shown in Figure 4. For every drop test, five pictures are shown and the corresponding time stamp in milliseconds is shown below the picture. Frame I shows the drop of hydrogen peroxide 5.5 ms prior to impact. In frame II, the first contact between fuel and oxidizer takes place which is defined as 0 ms. After impact, mixing of the fuel and oxidizer occurs. In frame III, the surface of the fuel oxidizer mixture breaks up and vapor is released. This is the first frame where vapor can be seen. It is not always very obvious in the snapshots, but quite clear in the video. The time difference between Frames II and III is referred to as the time to vapor generation. Figure 5 shows the determination of the time to vapor generation in more detail. Frame IV shows the ignition, which takes place in the vapor phase of all conducted drop tests. The ignition delay time is the time period from first contact until first appearance of a flame (the time difference between Frame II and IV). Frame V shows the flame propagation ca. 1 ms after ignition.

Snapshots with the monochrome high-speed recording of a drop test are shown in Figure 4 a). The fuel is BMIM, which was the first thiocyanate ionic liquid tested. Surprisingly ignition was achieved with the pure ionic liquid. This was not expected because only very few pure liquid substances react hypergolic

with H₂O₂. In Figure 4 a), the first contact of oxidizer and fuel is defined as 0 ms. At 35 ms after contact, vapor generation can first be observed. In this particular test the ignition takes place in the vapor phase at 43.5 ms after impact. After ignition is achieved in the vapor phase, the flame propagates and 1.5 ms after ignition the video is overexposed. The average ignition delay time of BMIM SCN and 96.1 % H₂O₂ is 45 ms. Figure 4 b) shows snapshots with the color high-speed recording of a drop test between H₂O₂ and EMIM SCN. In this drop test, vapor is generated after 28.3 ms and the ignition occurs at 32.2ms. The average ignition delay time for EMIM SCN is 31.7 ms.

The difference in ignition delay times between the two different cation structures of the thiocyanate ionic liquid is 11.3 ms on average. This is very similar to behavior of hypergolic ionic liquids with the dicyanamide anion and WFNA as oxidizer. Sun et al. [19] and McCrary et al. [47] investigated the influence of the cation structure of hypergolic ionic liquids on the ignition delay time. They found a difference in the ignition delay times between EMIM and BMIM cations on the order of 10 ms. As mentioned above, the hypergolic ignition of ionic liquids with oxidizers is mainly driven by the anion. Thus, the thiocyanate anion is responsible for the hypergolic ignition with hydrogen peroxide. The cation has an influence on the ignition delay as well as the physical and thermodynamic properties. It is possible that by changing the structure of the cation, that the ignition delay can be further reduced, similar to Sun et al. results [19].

Due to the fact that the ignition delay time of EMIM SCN is shorter than BMIM SCN, further investigations concentrated on the EMIM SCN. To lower the ignition delay, a catalytic additive was introduced to the ionic liquid fuel. Additives like dissolved copper salts can react highly catalytically on the decomposition of hydrogen peroxide [48]. The additive selected was copper (I) thiocyanate (Cu SCN), because solid salts have a good solubility in ionic liquids if they share the same anion [35].

Different concentrations of Cu SCN were dissolved in the EMIM SCN and investigated with the drop test. About 110 drop tests were conducted with the ionic liquid fuels. For each data point, at least six drop tests were performed to ensure repeatability of the ignition delay time. Moreover, the automated hypergolic drop test set up allows the user to conduct several drop tests with minimal effort after the syringe pump has been loaded with fuel and oxidizer. Table 3 lists the different concentrations of copper additive and the corresponding time to vapor generation (TVG), ignition delay time (IDT) with their standard deviations (SD), the number of conducted tests and the difference of the average IDT and TVG.

Table 3 Influence of copper additive on time to vapor generation and ignition delay time

| Additive content | Time to vapor generation | SD TVG | Ignition delay time | SD IDT | Difference between IDT and TVG | # of tests |
|------------------|--------------------------|--------|---------------------|--------|--------------------------------|------------|
|------------------|--------------------------|--------|---------------------|--------|--------------------------------|------------|

| [wt%] | [ms] | [ms] | [ms] | [ms] | [ms] | [ms] |
|-------|------|------|------|------|------|------|
| 0 | 28.3 | 4.2 | 31.7 | 4.2 | 3.4 | 30 |
| 0.5 | 17.0 | 0.8 | 19.3 | 0.6 | 2.3 | 6 |
| 1 | 14.9 | 1.8 | 16.2 | 2.0 | 1.4 | 23 |
| 2 | 14.3 | 1.8 | 15.7 | 1.9 | 1.4 | 8 |
| 3 | 14.5 | 1.7 | 15.6 | 1.7 | 1.1 | 7 |
| 5 | 13.1 | 1.7 | 13.9 | 1.8 | 0.8 | 24 |
| 7 | 15.5 | 1.5 | 16.4 | 1.2 | 0.9 | 7 |
| 10 | 16.3 | 1.2 | 16.9 | 1.0 | 0.6 | 6 |

The addition of 1 wt% Cu SCN reduces the ignition delay time to half that of the pure ionic liquid. An example ignition is shown in Figure 4 c). Figure 4 d) shows drop test with 5% copper additive. With this fuel, the minimum average ignition delay time in this test series is achieved with 13.9 ms on average. Also, the lowest absolute ignition delay time of 10.8 ms was measured for a fuel containing a 5% copper additive. A higher content of copper additive leads to an increase of the ignition delay once again. In Figure 4 c) to e), it can be seen that with an increasing copper additive content the flame turns greener and is more intense.

According to the literature [49-51], different phases in the hypergolic reaction are described. In the first phase, physical mixing processes are dominant and liquid chemical reactions begin to heat up the mixture. At some point the reaction rate increases drastically. This leads to a break-up of the surface of the fuel-oxidizer mixture and vapor is released. The ignition finally occurs in the vapor phase. Recently, Kang et al. provided an investigation regarding the different phases after initial contact until the ignition [51]. They differentiate between liquid phase reactions and gas phase reactions. The liquid phase reactions occur after initial contact of fuel and oxidizer. The gas phase reactions start, when visible vapor is emitted from the mixture. The phase, until an obvious vapor is generated, is referred to as the time to vapor generation in this study. The difference between time to vapor generation and ignition delay time corresponds to the length of the vapor phase reaction. The optical investigation enables the determination of the time when the first obvious vapor is generated and arises from the mixture. Figure 5 shows an example of a drop test with EMIM SCN in more detail especially the determination of the time to vapor generation. The first contact is defined as 0 ms. Between 25.8 ms and 26.1 ms the surface of the propellant mixture breaks up and vapor is released. This is determined in comparison of the single frames between 25.5 and 26.4 ms. The first vapor is visible at 26.1 ms and vapor generation increases afterwards. Hence, the time to vapor generation is in this test is 26.1 ms. The gas phase reactions occur and heat up the mixture until ignition can be seen at 30 ms after contact.

The time to vapor generation is also listed in Table 3. The TVG of the pure ionic liquid is 28.3 ms and decreases with the addition of the copper additive until 5 wt% copper additive. Higher copper contents

lead to an increase of the TVG. The difference between the average values of IDT and TVG, also displayed in Table 3, tends to decrease with higher copper contents. The shortest difference is determined for the fuel with 10% additive. This effect can also be seen in Figure 4 c) to e). Higher additive contents have a smaller amount of vapor release before ignition occurs.

3.3 Physical and thermal properties

Due to its highly reduced ignition delay time, the fuel consisting of EMIM SCN and 5 wt% Cu SCN was chosen for further investigation. The physical properties viscosity, density, and surface tension were measured. Thermogravimetric analysis and Fourier-transformed infrared spectroscopy (FTIR) were performed to further characterize the fuel component. These data were also collected for the neat EMIM SCN.

Table 4 Density (ρ), surface tension (σ), and viscosity (η) of ionic liquid fuels at 25°C

| Fuel | ρ [g/cm ³] | σ [mN/m] | η [mPa s] |
|----------------------------|--------------------------------|--------------------|-------------------|
| EMIM SCN | 1.11 | 46,3 ± 0,3 | 20.1 ± 0.1 |
| EMIM SCN + 5 wt% Cu SCN | 1.15 | 47,2 ± 0,1 | 29.6 ± 0.1 |

Table 4 lists the densities, viscosities, and surface tensions of the two ionic liquid fuels. By addition of 5 wt% Cu SCN to the pure ionic liquid fuel, fluid density is slightly increased. The impact on the surface tension between the pure ionic liquid and the catalytically promoted fuel is marginal. However, the viscosity of the fuel with an additive is increased by almost 50 %. This is in very good correlation with the published results of Zarcra et al. [35]. In contrast, the ignition delay time is reduced to the order of 50 % due to the addition of 5 wt% Cu SCN.

Thermogravimetric analysis (TGA) was conducted with the pure EMIM SCN liquid and the fuel mixture consisting of EMIM SCN and 5 wt% Cu SCN.

Figure 6 shows the normalized mass (black) and DSC signal (gray) corresponding to the temperature for both fuels. In the case of pure ionic liquid, the mass decreases rapidly starting from 210 °C, which means that the ionic liquid has begun to decompose. The onset decomposition temperature was determined at the intersection of the two dotted lines. The first line has is linear fitted to the TG curve between 30 and 190 °C. The second line is tangential at the inflection point of the fast decrease and has the highest gradient of the decrease. The intersection is at a temperature value of approx. 274.8°C. At 335 °C the mass is decreased down to only 2 % of the initial mass.

The beginning of additive-loaded fuel decomposition is shifted to higher temperatures (~230 °C) while the maximum decrease rate of the mass is higher compared to the pure ionic liquid. Therefore, the onset temperature determined as already described is at 272.2 °C. This is close to the onset temperature of the pure ionic liquid. At higher temperatures, the mass levels off to 6.4%. This is higher than the pure ionic liquid and induced by the additive. Under the given conditions, the copper is not able to react in an inert nitrogen atmosphere.

The DSC plots show negative curves during the thermal decomposition of the two fuels. This means the decomposition process is endothermic.

Figure 7 shows the FTIR analysis of the pure ionic liquid a) and the catalytically promoted fuel b). The characteristic absorption band of the thiocyanate functionality can be seen at 2046 1/cm. The difference between the two spectra is shown in Figure 7 c). It was calculated as the difference between the measured transmittance of fuel with catalytic additive and the pure fuel for every wavenumber $(\tilde{\nu})_i$.

$$\Delta(\tilde{\nu})_i = \text{transmittance}_{EMIM\ SCN + 5\% Cu\ SCN}(\tilde{\nu})_i - \text{transmittance}_{EMIM\ SCN}(\tilde{\nu})_i \quad (5)$$

Around the characteristic absorption band of the thiocyanate functionality a difference of single transmittance values can be seen. In Figure 7 d) the thiocyanate region is shown in more detail. It is obvious that the addition of copper ions influences the characteristic absorption band. Such an effect was also described by Cabeza et al. [52] and their investigation of ionic liquids containing complex metal thiocyanate anions. They found a double peak in the IR spectrum of copper thiocyanate ionic liquid at 2052 and 2069 1/cm. The formation of a copper thiocyanate complex is very likely to happen by dissolving the copper thiocyanate in the EMIM SCN. The result is an ionic liquid containing EMIM⁺ cation, SCN⁻, and complex copper thiocyanate anions.

3.4 Evaluation of ignition delay time

In the presented test results, the absolute and average ignition delay times of the additive promoted fuels have a minimum at 5 wt% copper additive. The presented dataset indicates that there is no further significant reduction of ignition delay time for higher copper contents than 5% additive. In the contrary, for higher additive contents the ignition delay time increases again. This was surprising, because it was expected that the hypergolic reaction is driven by the copper additive and faster ignitions are observed with higher additive contents.

The conducted measurements show that for higher copper additive contents the viscosity increases significantly. Whereupon the thermal behaviour and surface tension become similar. Zarca et al.

characterized the viscosity of EMIM SCN and Cu SCN mixtures for a wide range additive concentration and temperatures [35]. These results indicate that the viscosity of the fuel with 10% additive at 25°C would be close to 50 mPa s, which is 2.5 times of the initial viscosity. For higher copper concentrations the period of the vapor phase reactions is decreased. The time to vapor generation, where mixing of fuel and oxidizer occurs, is increasing for higher additive concentrations (>5 wt%). This suggests that the mixing processes are influenced by the increasing viscosity for higher copper contents. For the fuels with more than 5 wt% additive content, the mixing is impeded because of the higher viscosity. This effect supersedes the increased reaction rate due to the high amount of catalytically promoter. The adverse effect of higher viscosities on the ignition delay time in drop tests was also described by Ladanyi and Miller [53].

In literature, different values for ignition delay time of hypergolic fuels can be found, which are reported to be sufficient for smooth ignition of a combustion chamber. Drop test results of common hypergolic propellants like MMH/NTO have an ignition delay on the order of a millisecond [14]. Rapid reproducible ignitions in a combustion chamber have been demonstrated with a hypergolic green propellant with an ignition delay in the drop test of 15 ms [54]. For a later possible application of green propellants in thrusters, the ignition delay time of 13.9 ms at 5 wt% additive content could be sufficient to achieve fast, repeatable, and smooth ignitions. But the presence of metallic additives can have the aforementioned adverse effects such as I_{sp} reduction and formation of solid particles. The addition of a smaller amount of 1 wt% copper additive cuts the ignition delay time nearly in half. Possibly this IDT could also be sufficient for smooth ignitions in a combustion chamber. This also would reduce the adverse impact related to the metallic fuel component. Furthermore, the demonstrated hypergolicity of pure thiocyanate ionic liquids implies that other thiocyanate ionic liquids may be hypergolic too. This offers the possibility to lower the ignition delay by “tuning” the structure of the cation.

The drop test is a suitable tool to examine reactivity of different propellant components. But ignition delay values of drop tests are not representative for combustion chambers. Therefore, ignition testing under flowing conditions using injectors and a combustion chamber are necessary to validate the results of the drop test and to evaluate the performance of the propellants under relevant conditions. This will be conducted in further investigations at the DLR.

4 Conclusion

Ionic liquids with the thiocyanate anion were studied as potential hypergolic fuels with highly concentrated hydrogen peroxide. These ionic liquids offer low melting points, moderate viscosities, and are proven to be hypergolic with WFNA on the order of several 100 ms.

In a first step, the theoretical performance of two different green propellant combinations was calculated. The propellants consist of 98% hydrogen peroxide as oxidizer and two commercially available ionic liquids served as fuel, 1-ethyl-3-methylimidazolium thiocyanate and 1-butyl-3-methylimidazolium thiocyanate. The theoretical I_{sp} calculated with NASA CEA ($\epsilon=330$, $p_c=10$ bar, frozen expansion) for the two ionic liquids is roughly 318s. Due to the higher fuel density, the density specific impulse is around 430 s kg / m^3 . This is a 10 % improvement compared to the conventional hypergolic propellant combination of MMH/NTO.

Drop tests with the two ionic liquids and hydrogen peroxide were conducted. Both ionic liquids showed hypergolic behavior with hydrogen peroxide at a concentration of 96.1%. Ignition delay times were 31.7 ms on average for EMIM SCN and 45 ms for BMIM SCN. A catalytic additive was dissolved in the EMIM SCN in order to lower ignition delay times. The promoted fuels with different amounts of Cu SCN were also investigated in the drop tests. A minimum ignition delay time of 13.9 ms was determined for the fuel at a 5 wt% Cu SCN concentration. For higher additive contents the ignition delay time rose again slightly. The time to vapor generation was also determined. The time period of the gas phase reaction decreases with higher copper additive content. Due to lowest ignition delay the mixture of EMIM SCN with 5 wt% Cu SCN was chosen for further investigation.

Thermogravimetric analysis and Fourier-transformed infrared spectroscopy (FTIR) were performed as well as density, viscosity, and surface tension measurements. The results were compared to the basic ionic liquid. The viscosity is increased from 20 mPa to 29 mPa s by the addition of 5 wt% Cu SCN. The change in density and surface tension is marginal. The onset temperature of the endothermic decomposition of the pure ionic liquid fuel and the catalytically promoted fuel are both fuel are in the range of 273-275 °C. The FTIR spectra indicate that a complex copper thiocyanate anion is formed by the addition of the catalytic additive.

In conclusion, thiocyanate ionic liquids were found to be hypergolic with highly concentrated hydrogen peroxide with a short ignition delay on the order of tens of milliseconds. This is a significant finding, because only very few pure substances are hypergolic with hydrogen peroxide. Furthermore, the calculated performance of the ionic liquids in terms of I_{sp} and ρI_{sp} is close or better than the conventional toxic propellants. Therefore, thiocyanate ionic liquids and hydrogen peroxide are very promising replacement candidates for the current hypergolic propellants in orbital propulsion systems.

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Declaration of interest

A patent application on hypergolic thiocyanate propellants is pending

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Figures:



Figure 1 Ionic liquid based fuels

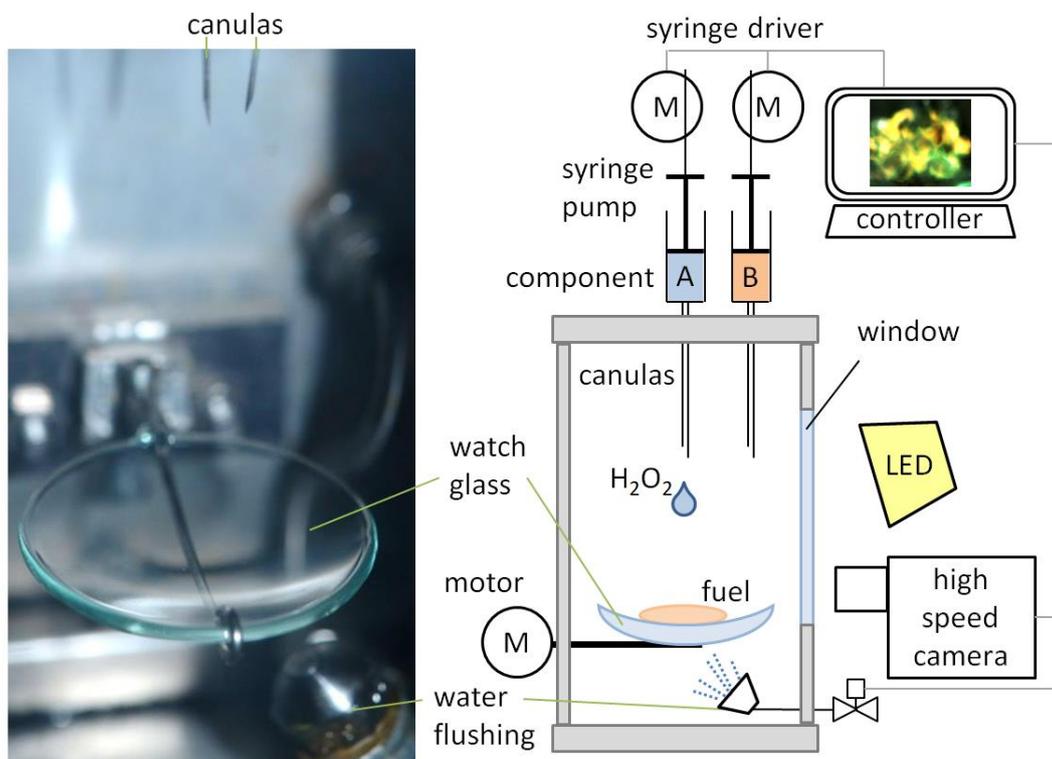


Figure 2 Automated hypergolic drop test setup: photo of the inside (left), scheme (right)

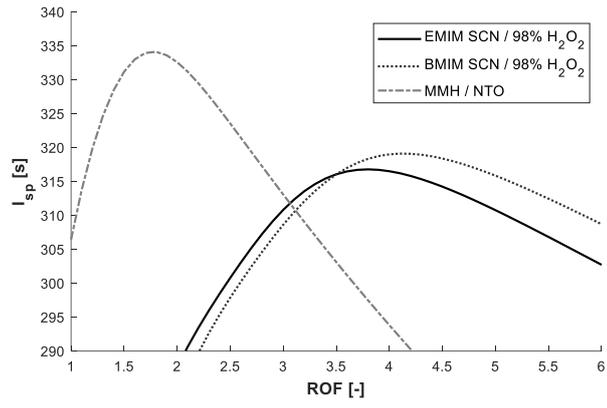


Figure 3 I_{sp} over ROF conventional propellant vs ionic liquid H₂O₂ combination. Theoretical values, assuming frozen supersonic expansion, ϵ : 330, p_c : 10 bar

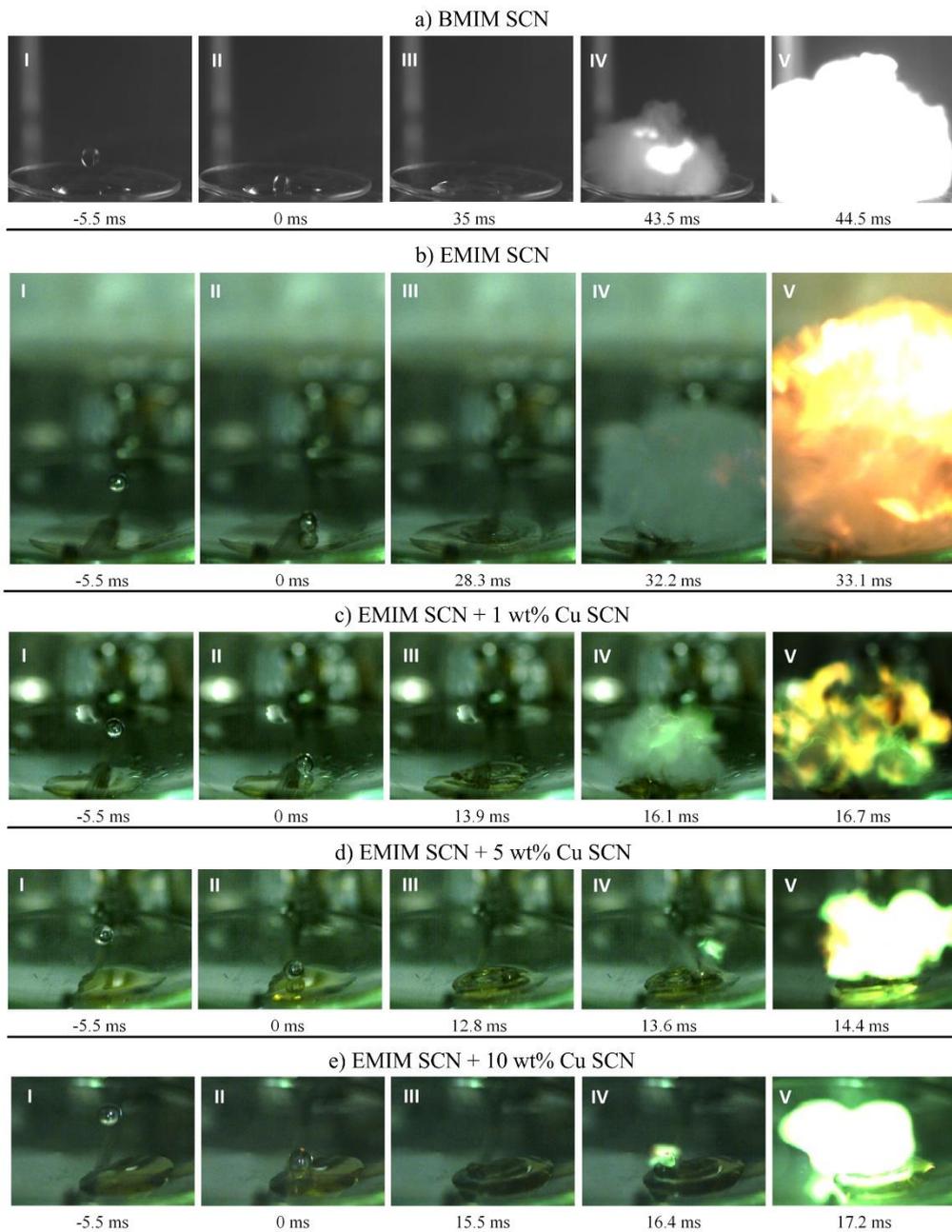


Figure 4 Comparison of hypergolic ignition of different fuels with 96.1 % hydrogen peroxide in drop tests.

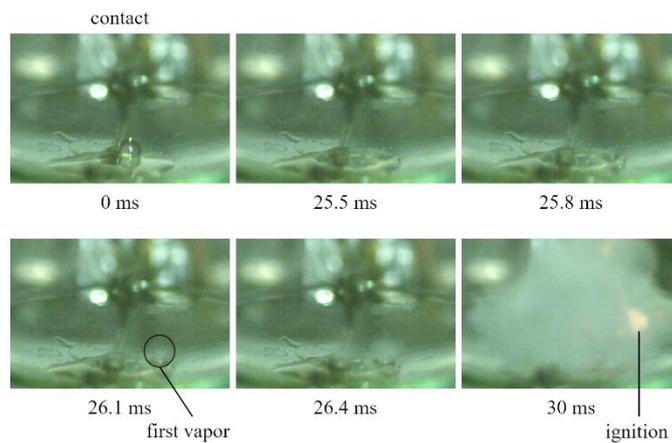


Figure 5 Determination of TVG and IDT

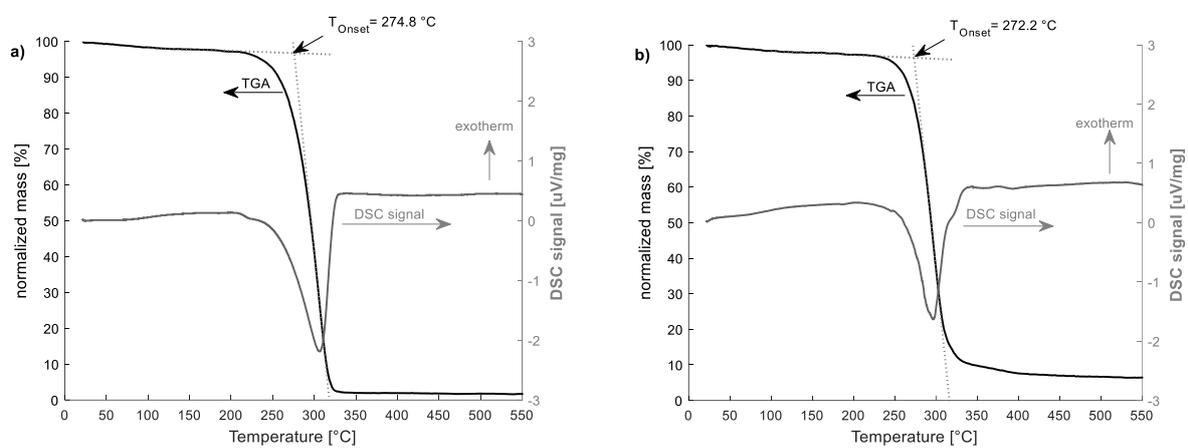


Figure 6 TG/DSC curves of a) EMIM SCN and b) EMIM SCN+5 % Cu SCN

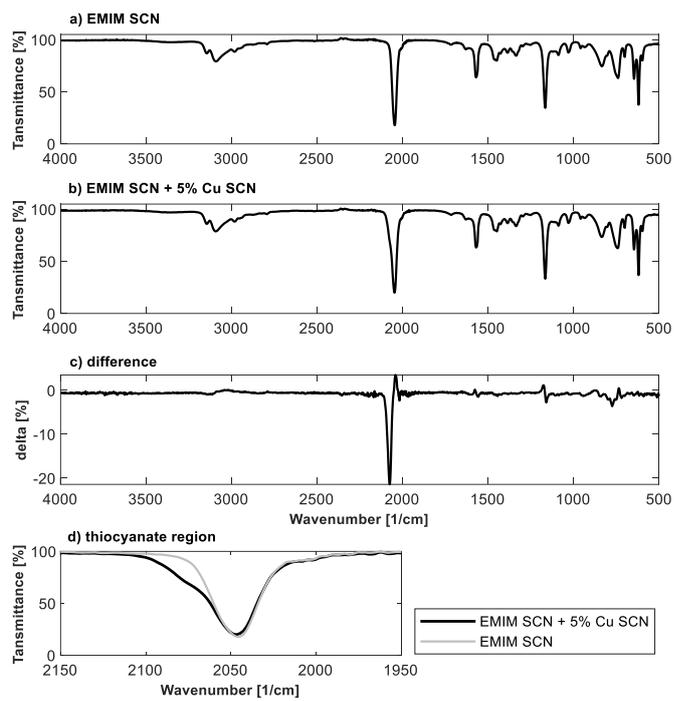


Figure 7 FTIR spectra of a) pure EMIM SCN, b) EMIM SCN + 5% Cu SCN, c) the difference between of the two spectra, d) thiocyanate region

Figure Captions:

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