Co-Electrolysis-Assisted Decomposition of Hydroxylammonium Nitrate–Fuel Mixtures Using Stainless Steel–Platinum Electrodes

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ABSTRACT: Hydroxylammonium nitrate (HAN) is a promising green propellant because of its low toxicity, high volumetric specific impulse, and reduced development cost. Electrolytic decomposition of HAN is an efficient approach to prepare it for further ignition and combustion. This paper describes the investigation of a co-electrolysis effect on electrolytic decomposition of HAN–fuel mixtures using stainless steel–platinum (SS–Pt) electrodes. For the first time, different materials were utilized as electrodes to alter the cathodic reaction, which eliminated the inhibition effect and achieved a repeatable and consistent electrolytic decomposition of HAN solution. Urea and methanol were added as fuel components in the HAN–fuel mixtures. When the mass ratio of added urea \( \geq 20\% \), the electrolytic decomposition of a HAN–urea ternary mixture achieved 67% increment in maximum gas temperature \( (T_{g\text{max}}) \) and 185% increment in overall temperature increasing rate over the benchmark case of HAN solution. The co-electrolysis of urea released additional electrons into the mixtures and enhanced the overall electrolytic decomposition of HAN. In contrast, the addition of methanol did not improve the \( T_{g\text{max}} \) but only increased the overall temperature increasing rate. This work has important implications in the development of an efficient and reliable electrolytic decomposition system of HAN and its mixtures for propulsion applications.

INTRODUCTION

In the effort of replacing toxic hydrazine, which is commonly used as a liquid propellant in chemical propulsion systems, hydroxylammonium nitrate (HAN) attracts wide research interests due to its low toxicity and reduced development cost. HAN has similar specific impulse but higher density than hydrazine. The resultant higher density-specific impulse ratio is beneficial to the applications in volume-constrained propulsion systems, such as those used in nanosatelites.

Thermal and catalytic decomposition of HAN are the two commonly employed techniques. Though the reaction mechanisms for both techniques are similar at atmospheric pressure, the catalytic technique can reduce the onset temperature of HAN decomposition. An iridium-based catalyst has an activated reaction path of nitric acid generation, which is a primary liquid phase reaction. The catalyst is reversibly damaged during the high-temperature operation and the thermal runaway caused by the autocatalytic reaction could severely damage the propulsion system. The issue of increased heat loss due to a high surface area to volume ratio at microscale, coupled with catalyst deactivation, suggested that the conventional thermal and catalytic techniques are unfavorable for application in a micropropulsion system.

Electrolytic decomposition has been proposed as an alternative decomposition method of HAN due to its ionic liquid nature. In this method, a series of electrochemical reactions was initiated to decompose the HAN propellant with an applied electrical potential. Numerous studies on HAN-based liquid propellants have been conducted to understand the reaction mechanisms involved. Metal-based materials, such as titanium, copper, aluminum, silver, etc., have been employed as an electrode in the electrolytic decomposition of the HAN propellant. However, the gaseous products released during the decomposition have created a strong oxidizing environment, which consumed the electrodes. In spite of their effectiveness in initiating electrolytic decomposition of HAN-based liquid propellants, the sacrificial nature of metal electrodes remains a major concern and might limit the lifespan of micropropulsion systems. Therefore, noble metal, i.e., platinum, was investigated as a potential electrode material to prevent electrode consumption, yet maintaining the effectiveness of electrolytic decomposition of the HAN-based liquid propellant.

The HAN–fuel mixtures that were being studied extensively till date are LP 1846 (a mixture of HAN, triethylammonium nitrate (TEAN), and water at 60.8/19.2/20 wt %) and SHP 163 (a mixture of HAN, methanol, ammonium nitrate, and water at 73.6/16.3/3.9/6.2 wt %). Methanol could suppress the high linear burning rate of HAN solution effectively but the decomposition mechanisms of HAN
solution were reported to change with the addition of methanol.24 Such changes might complicate the understanding of the decomposition mechanisms of HAN propellants. Thus, a search for an alternative fuel component, which is more suitable for electrolytic decomposition of HAN is required. Although electrolytic decomposition of HAN–water solution was modeled similarly to the thermal decomposition process,10 the underlying reaction mechanisms involving fuel are still unclear.

In this study, the electrolytic decomposition of HAN solution was first investigated using three electrode combinations in an insulated glass reactor to identify the optimal electrode combination for subsequent studies. Then, the effect of co-electrolysis of two selected fuel components, i.e., methanol and urea, on the electrolytic decomposition of a HAN ternary mixture has been studied using absorption spectroscopy and calorimetry. The obtained analytical results have been analyzed to determine the reaction mechanisms involved in the electrolytic decomposition of HAN–fuel mixtures.

![RESULTS AND DISCUSSION](http://pubs.acs.org/doi/abs/10.1021/acsomega.0c01804)

**HAN–Fuel Mixture Characterization.** Fourier transform infrared (FTIR) spectra of a HAN solution, HAN–urea mixture, and HAN–methanol mixture are shown in Figure 1.

![Figure 1. FTIR spectra of HAN solution, HAN–urea, and HAN–methanol at the selected fuel ratio.](http://pubs.acs.org/doi/abs/10.1021/acsomega.0c01804)

The FTIR spectra for HAN solution are similar to those obtained previously.25,26 The bands located at 1157, 1471, 1602, 1632, 1660, 3373, and 3477 cm\(^{-1}\) are assigned to urea in HAN–urea by analogy with urea solution used.27 The band located at 2844 cm\(^{-1}\) is assigned to methanol in HAN–methanol by analogy with methanol used.28 The results obtained are tabulated in Table 1 and are in good agreement with literature values, indicating successful mixing of HAN with other fuel components.

**Table 1. Vibration Frequencies Corresponding to Different Species in HAN, HAN–Urea, and HAN–Methanol**

| species   | wavenumber, cm\(^{-1}\) |
|-----------|--------------------------|
| NH\(_3\)OH\(^+\) | 1007, 1193, 1520, 1762, 2737, 2984, 3161 |
| NO\(_3\)\(^-\) | 1040, 1339, 1393 |
| water     | 1613, 3416, 3569 |
| urea      | 1157, 1471, 1602, 1632, 1660, 3373, 3477 |
| methanol  | 2844 |

![HAN Solution Decomposition Using Different Electrodes.](http://pubs.acs.org/doi/abs/10.1021/acsomega.0c01804)

**Table 2. Details of Electrode Materials Used During Electrolytic Decomposition of 80 wt % HAN Solution**

| set | cathode       | anode       |
|-----|---------------|-------------|
| 1   | platinum      | platinum    |
| 2   | stainless steel| stainless steel |
| 3   | stainless steel| platinum    |

cathodes and anodes, respectively. To identify the optimum electrode pair for a subsequent electrolytic decomposition study, the decomposition profile of HAN solution using different electrode material combinations were evaluated. The corresponding temperature evolutions as a function of time for electrolytic decomposition of 80 wt % HAN solution using different electrode pair combinations are presented in Figure 2.

Electrolytic decomposition was initiated when a potential voltage of 60 V was applied, as indicated by the increase in the evolved current and measured gas temperature. Platinum electrodes and stainless steel–platinum (SS–Pt) electrodes displayed a rather similar decomposition profile. Stainless steel electrodes, on the other hand, had a negligible temperature increase in the first 10 s and displayed a rapid increase in measured gas temperature thereafter. From these results, it was seen that the highest measured gas temperature of 147 °C was obtained with stainless steel electrodes.

While all of the electrode material combination pairs were able to electrolytically decompose the HAN solution in the first test, the decomposition profile using platinum (Pt) and stainless steel (SS, SS 316) electrodes became inconsistent after a few repeated experiments, despite the fact that platinum exhibited a catalytic effect toward HAN decomposition.8 In a typical repeating experiment, when using the SS (SS–Pt) and Pt (Pt–SS–Pt) electrodes, the evolved current increased to a maximum as the voltage was applied. In case of using Pt electrodes, the current dropped to a minimum of 0.2 A after 2 s. On the other hand, the current dropped to a minimum and fluctuated in case of using SS electrodes. Since then, the electrolytic decomposition has stalled, even if the power supply remains switched on. To achieve a full electrolytic decomposition of HAN solution, multiple applied electric potentials, i.e., switching on and off the power supply alternatively, were required.

From the drop in the electrical current drawn by the electrolytic reaction and negligible increase in gas temperature, it can be deduced that there is an inhibition effect toward
continuous decomposition of HAN solution. Such an effect can be explained by the adsorption phenomenon of nitrate ions on the electrode surface. When Pt electrodes are used, nitrate reduction can only occur at potential values when evolution of hydrogen gas is high.\textsuperscript{29,30} Thus, the low enthalpy of nitrate reduction over platinum, when compared to hydrogen, resulted in nitrate ions unable to competitively adsorb onto the electrode surface.

The inhibition effect ceased the decomposition of HAN and resulted in a large deviation in the measured gas temperature. As such, repeatability of the reaction poses a problem if Pt and SS are used as electrode materials in the micropropulsion system. Hence, these two materials are deemed unsuitable for use in electrolytic decomposition of HAN-based propellants.

The nickel content in stainless steel could promote the nitrate reduction over platinum in acidic media.\textsuperscript{31} Thus, stainless steel was chosen as a cathode for electroreduction of nitrate to prevent such an inhibition effect. While the SS–Pt electrode pair was not affected by the inhibition effect, further testing on its durability in extended operation was necessary. Repeated trials were carried out using the same SS–Pt electrode. The percentage of mass change in SS–Pt electrode was measured to be very small, at most 0.025% after one trial (Figure S1). The temperature and current profiles of these trials also showed a similar trend (Figure S2) with no obvious deviation. All of these results, i.e., absence of the inhibition effect, low mass loss, and consistent reaction profiles, suggest that SS–Pt electrode pair could be a better material combination for use as an electrode in electrolytic decomposition of HAN propellants. Thus, SS–Pt electrodes were used in the subsequent studies on a HAN–fuel mixture.

**Electrolytic Decomposition of HAN–Urea Mixtures Using SS–Pt Electrodes**. The temperature profiles with corresponding evolved current during the electrolytic decomposition of HAN solution and selected a HAN–fuel mixture using SS–Pt electrodes are depicted in Figure 4. Electrolytic decomposition of HAN solution demonstrated a linear increase in temperature from room temperature to a maximum temperature of 120 °C. This represents a single-stage decomposition, which is consistent with the results reported in previous studies.\textsuperscript{12,13}

For HAN–20% urea, it showed a rather similar temperature increase and current profile as HAN solution until 13 s. Thereafter, the measured gas temperature increased abruptly to a maximum of approximately 200 °C. Such a high measured gas temperature implies that the addition of urea facilitated the electrolytic decomposition of HAN, which is an exothermic process. Previous work has shown that additional electrons are essential to enhance electrolytic decomposition of HAN.\textsuperscript{12} In this case, the additional electrons originating from the electrolysis reaction of urea,\textsuperscript{32} as given in eq 1, enhanced the overall reaction.

\[
\text{anode: CO(NH}_2\text{)}_2 + 6\text{OH}^- \rightarrow \text{N}_2 + 5\text{H}_2\text{O} + \text{CO}_2 + 6\text{e}^- \\
\text{cathode: } 6\text{H}_2\text{O} + 6\text{e}^- \rightarrow 3\text{H}_2 + 6\text{OH}^- \\
\text{overall: } \text{CO(NH}_2\text{)}_2 (aq) + \text{H}_2\text{O} (l) \rightarrow \text{N}_2 (g) + \text{H}_2 (g) + \text{CO}_2 (g)
\]

Simultaneously, urea was thermally decomposed and hydrolyzed to produce ammonia in a two-step reaction, according to eq 2,\textsuperscript{34} as the temperature elevated and in the presence of water in the mixture. Ammonia then underwent electrolysis,\textsuperscript{34} eq 3, to release even more electrons into the mixture.

\[
\text{thermolysis: CO(NH}_2\text{)}_2 \rightarrow \text{NH}_3 + \text{HNCO} \\
\text{hydrolysis: HNCO + H}_2\text{O } \rightarrow \text{NH}_3 + \text{CO}_2 \\
2\text{NH}_3 \rightarrow 2\text{N}_2 + 6\text{H}^+ + 6\text{e}^-
\]

After approximately 17 s, the measured current for electrolytic decomposition of HAN–urea reached a minimum of 0.5 A before continuously increasing to a steady value of 1.15 A for an extended time. In contrast, the measured current decayed to a near zero value in the later stage of electrolytic decomposition of HAN solution. Such an observation suggests that the continuous production of electrons from electrolysis of urea sustained the electrolytic decomposition of HAN and urea for a longer time. This is evidenced by (1) the measured gas temperature that remained higher than 100 °C throughout the 60 s of the measurement and (2) the trace of ammonium ions from the FTIR analysis in the remaining mixture in the glass reactor.

As shown in Figure 5, the remaining mixture of HAN solution showed a characteristic peak for nitrate at 1339 and 1393 cm$^{-1}$ and water at 1613 and 3413 cm$^{-1}$, respectively. The

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**Figure 3.** Inhibition effect shown by HAN solution decomposition using (a) stainless steel and (b) platinum electrodes. The squared voltage reading refers to the duration of applied potential difference from the power supply.

**Figure 4.** Decomposition profiles of HAN solution and HAN–urea mixture.

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FTIR spectra of the remaining mixture from HAN−urea experiment indicate the presence of an ammonium ion at 1440 cm$^{-1}$, which is attributed to the dissolved ammonia, produced from eq 2, in the water to give an ammonium ion, according to eq 4. A comparison of FTIR spectra confirms that the remaining residual is ammonium nitrate (NH$_4$NO$_3$).

$$\text{NH}_4 \text{(g)} + \text{H}_2\text{O (l)} \leftrightarrow \text{NH}_4\text{OH (aq)} \quad (4)$$

To investigate the co-electrolysis effect further, the reaction was stopped at 12 and 20 s, followed by an FTIR analysis immediately. The time at 12 s represents the moment before peak temperature was achieved in the electrolytic decomposition of the HAN−urea mixture, while 20 s is the moment when the measured temperature stopped dropping and sustained until the end of the reaction.

From Figure 6a, no trace of an ammonium ion (NH$_4^+$) is detected in the as-prepared HAN−urea mixture. However, the ion appears after the electrolytic decomposition started (for cases of 12 s, 20 s, and the end of the reaction). This validates the occurrence of thermolysis and hydrolysis of urea into ammonia, which is subsequently electrolyzed and dissolved as ammonium ions, as suggested previously in eqs 2 and 4.

The FTIR result in Figure 6b shows the presence of a hydroxylammonium ion, NH$_3$OH$^+$, (1007 cm$^{-1}$) at 12 s but disappearance at 20 s in electrolytic decomposition of the HAN−urea mixture. Based on these analytical results, it can be deduced that co-electrolysis of HAN and urea is dominant in the first half of the reaction, where HAN is rapidly consumed to release a large amount of thermal energy. After the hydroxylammonium ions are consumed, the reaction is sustained by the electrolysis of ammonium nitrate, which continuously releases thermal energy until the mixture is depleted. This is notably different if compared to the case of HAN solution, where the electrolytic reaction is dominant in the first half of the reaction and thermal decomposition takes over thereafter, but appeared to be similar to thermal decomposition of LP 1846, where reactions of HAN and TEAN occurred first, followed by the TEAN reaction only.

**Electrolytic Decomposition of HAN−Methanol Mixtures Using SS−Pt Electrodes.** Electrolytic decomposition of HAN−20% MeOH behaves rather differently from HAN solution, as shown in Figure 7. The measured gas temperature increased to about 70 °C from the initial temperature and continued to increase at a low rate to 105 °C. The difference in the HAN−20% MeOH decomposition was also observed in its current profile. Both HAN−MeOH mixture and HAN solution had a similar current trend between 0 and 2 s. After 2 s, the measured current for HAN solution started to drop. However, an increase in the measured current was observed in the case of HAN−20% MeOH. After achieving the maximum value of 3 A at 6 s, the measured current started to decrease as well.

The anodic reaction for electrolysis of methanol and water produces six and two electrons, respectively, according to eq 5. This explains the larger current drawn, as observed in the early stage of the reaction for HAN−20% MeOH in Figure 7.

methanol: \[
\text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 6\text{H}^+ + 6\text{e}^-
\]

water: \[
\text{H}_2\text{O} + 0.5\text{O}_2 + 2\text{H}^+ + 2\text{e}^-
\]

After attaining its maximum gas temperature at approximately 20 s, both the measured temperature and current...
profiles for HAN–20% MeOH showed a similar decreasing trend as HAN solution. This led to the conclusion that the electrochemical reactions in the later stage of reactions for HAN–20% MeOH and HAN solution were similar, and the methanol was consumed in the early reaction. This is further validated by the FTIR analysis of the remaining mixture from the electrolytic decomposition of the HAN–20% MeOH mixture. The FTIR profile of HAN–20% MeOH is similar to HAN solution, as shown in Figure 8.

Figure 8. FTIR spectra of HAN–20% MeOH and HAN solution after decomposition using SS–Pt electrodes.

Electrical energy put into the HAN–fuel mixture at different fuel ratios using SS–Pt electrodes are shown in Figure 9. For HAN–methanol, the energy consumed is higher than that of HAN solution but stays rather constant even when the fuel ratio is different. This is consistent with the above discussion that methanol does not promote the electrolytic decomposition of HAN. In contrast, the energy put into the HAN–urea mixture increases linearly with the fuel ratio. This linear correlation, again, proves that the addition of urea enhances the electrolytic decomposition of HAN via the co-electrolysis effect, which draws more electrical current from the power supply.

Comparison of Electrolytic Decomposition Performance of Different HAN–Fuel Mixtures. Understanding the decomposition performance of the HAN–fuel mixture at different fuel ratios has significant implications, as the optimum HAN–fuel mixture can be determined. The maximum gas temperatures, $T_{g_{max}}$ obtained during the decomposition of the HAN–fuel mixture at different fuel ratios using SS–Pt electrodes are illustrated in Figure 10. 0% refers to the benchmark HAN solution without any addition of fuel.

Figure 10. Maximum measured gas temperature of HAN solution and HAN–fuel mixtures at different fuel ratios.

For a HAN–methanol mixture, the $T_{g_{max}}$ obtained is rather similar for all fuel ratios. It is expected as the methanol does not facilitate the electrolytic decomposition of HAN, as observed in the cases where urea is added. The fluctuation in measured $T_{g_{max}}$ is mainly due to the induced hydrodynamic instability after adding the methanol to HAN solution. For a HAN–urea mixture, the $T_{g_{max}}$ obtained does not exceed the benchmark when the fuel ratio is less than 20%. The $T_{g_{max}}$ increases abruptly when the fuel ratio is 20% and above, where the increment can be as high as 67% over the benchmark case. It is anticipated that more heat energy is generated by the enhanced electrolytic decomposition of HAN as a result of additional electrons from electrolysis of urea, as discussed in the Electrolytic Decomposition of HAN–Urea Mixtures Using SS–Pt Electrodes section. However, the hydrolysis reaction of urea is an endothermic process. Part of the additional heat energy generated is compensated, thus, the increase in $T_{g_{max}}$ is almost negligible for the low urea ratio. As the added urea ratio exceeds the 20% threshold, it gives a net increase in heat energy, therefore an increase in $T_{g_{max}}$ as well.

The overall temperature increasing rate of electrolytic decomposition of HAN–fuel mixtures is depicted in Figure 11. In general, addition of a fuel component increased the overall temperature increasing rate. For low fuel ratios (10 and 15%), the increase in the overall temperature increasing rate is insignificant. For the HAN–20% urea mixture, the overall temperature increasing rate surged, and it is approximately 185% higher than the case without the addition of urea. By FTIR analysis of the HAN–urea mixtures, as shown in Figure 12, a broad peak was observed at the regime of 3300–3500 cm$^{-1}$ for the HAN–15% urea mixture. However, the broad peak was separated into two smaller and distinct peaks as the fuel ratio increased beyond 20%, showing the antisymmetric and symmetric stretching bands of NH$_3$ at 3379 and 3482 cm$^{-1}$. This shows the dominating presence of a NH$_3$ group in the HAN–urea mixture at such a ratio, which functions...
similarly to NH₂OH, and therefore explaining the rapid increase in the $T_{g_{\text{max}}}$ and the overall temperature increasing rate.

**CONCLUSIONS**

In this study, the inhibition effect in electrolytic decomposition of HAN solution was discovered when platinum and stainless steel were used as electrodes. The effect has a negative impact on the repeatability of the electrochemical reaction of HAN solution. Using stainless steel as a cathode and platinum as an anode, such an effect was eliminated with a repeatable and consistent electrolytic decomposition of HAN solution demonstrated.

Subsequently, this electrode combination pair (SS–Pt) was used to investigate the electrolytic decomposition of the HAN–fuel mixture with varying fuel ratios, between 10 and 30%, in an insulated glass reactor. The fuel components studied are urea and methanol. FTIR results showed successful preparation of HAN–urea and HAN–methanol ternary mixtures.

Reaction kinetics for electrolytic decomposition of the HAN ternary mixture with addition of different fuel components is vastly different. FTIR results on the remains of HAN–urea suggests that the electrolysis of urea lasts until the end of the overall electrolytic decomposition reaction. The co-electrolysis effect is particularly remarkable when the urea ratio is 20% and above. Additional electron release from the electrolysis of urea facilitated and enhanced the electrolytic decomposition of HAN. It leads to 67% higher $T_{g_{\text{max}}}$ and 185% higher overall temperature increasing rate than the benchmark case of HAN solution.

Improvements in $T_{g_{\text{max}}}$ were not observed when methanol was added as a fuel component. The overall temperature increasing rate of HAN–MeOH samples was higher than that of HAN solution but 15.5% lower than HAN–urea on average. FTIR spectra of remaining HAN–methanol suggests that the reaction is initially electrolytic dominant, then progresses into thermal decomposition as the methanol is consumed.

The positive implications toward propulsion applications are demonstrated by consistent HAN decomposition achieved using an SS–Pt electrode pair and improved HAN decomposition with fuel addition.

**EXPERIMENTAL SECTION**

**HAN–Fuel Mixtures Preparation.** HAN solution was prepared in-house via a controlled reaction between diluted aqueous solutions of nitric acid (Sinopharma, China) and hydroxylamine (Huaxia, China), according to eq 6. Further details of HAN solution synthesis are described in our previous work.\(^\text{25}\)

\[
\text{NH}_2\text{OH} \text{(aq)} + \text{HNO}_3 \text{(aq)} \rightarrow \text{NH}_2\text{OHNO}_3 \text{(aq)} 
\]

After purification using a rotary evaporator under vacuum condition, the concentration of HAN solution was 80 wt %, which was determined by the density correlation method,\(^\text{26}\) according to eq 7.

\[
\rho = \frac{107.85}{(96.042 - 30.99 \omega_{\text{HAN}})} 
\]

where $\rho$ is density of HAN solution (g/cm³) and $\omega$ (HAN) is the mass concentration of HAN solution.

In this study, urea (Yuanye, China) and anhydrous methanol (MeOH) (Macklin, China) were selected as the fuel components for the HAN–fuel mixture. The mass of HAN solution was fixed at 1 g. The maximum ratio of the fuel component to HAN solution was selected based on the solubility limit of fuel in HAN solution, which is 30% for the solubility of urea in HAN solution. The amount of fuel component to HAN solution was thus varied between 10 and 30%. Table 3 summarizes the detailed information of the two HAN–fuel mixtures used in this study.

**Table 3. Synthesized HAN–Fuel Mixture Ratio (Fuel: Urea or Methanol) and Calculated Oxygen Balance**

| Fuel Mixture Ratio (Fuel: Urea or Methanol) | Initial Mass, g | Fuel Mass, g | Final Mass, g | Oxygen Balance, % (methanol: urea) |
|-------------------------------------------|-----------------|--------------|---------------|-------------------------------------|
| HAN                                       | 1               | 0.00         | 1.00          |                                     |
| HAN–10% fuel                              | 1               | 0.10         | 1.10          | 10.60; 16.95                        |
| HAN–15% fuel                              | 1               | 0.15         | 1.15          | 3.62; 12.74                         |
| HAN–20% fuel                              | 1               | 0.20         | 1.20          | -2.77; 8.88                         |
| HAN–25% fuel                              | 1               | 0.25         | 1.25          | -8.65; 5.33                         |
| HAN–30% fuel                              | 1               | 0.30         | 1.30          | -14.08; 2.05                        |

**HAN Propellants Electrolytic Decomposition.** Electrolytic decomposition of HAN propellants was conducted in a double-layer vacuum insulated glass reactor under atmospheric conditions. The vacuum between the internal and external glass walls could mitigate the heat loss due to convection effectively. A pair of metal electrodes (4 mm outer diameter) was mounted at a fixed separation, and a glass tube for the gas exhaust was inserted between the electrodes, which were held together with a silicone stopper, as illustrated in Figure 13. To
remove impurities prior to immersion, electrodes were cleaned and rinsed with ultrapure water. The gas exhaust temperature was measured using a K-type thermocouple (RSPro, 1 mm outer diameter, U.K.) for calorimetric analysis. The applied voltage, evolved current, and gas-phase temperature were recorded during the decomposition of HAN propellant at a sampling rate of 10 Hz using a data logger (Graphitec, GL240, Japan).

In a typical experiment, the HAN propellant was prepared right before experiment and was profiled in the reactor. The stopper was applied to the reactor so that the exhaust gas was directed. Decomposition of the propellant was achieved by applying electrical energy from a DC power supply unit (Asstpower, DML60-25, China). A constant voltage of 60 V was applied in each trial while the maximum allowable current drawn was capped at 5 A. After the test, the reactor was dismounted, cleaned, and set up again for another test. The current was applied in each trial while the maximum allowable current was drawn was capped at 5 A. After the test, the reactor was dismounted, cleaned, and set up again for another test. The length of the electrode immersed in HAN solution was 0.5 cm.

FTIR Analyses. The chemical species of the HAN solution and HAN—fuel mixture were identified using FTIR analysis (Thermo Scientific, Nicolet iS10). A calcium fluoride (CaF₂) cell was chosen as a sample cell due to its strong tolerance to water and high optical transmittance. The analyses of the liquid samples were performed with the two CaF₂ cells between stainless steel holders using the liquid film method. As CaF₂ has an optical transmission wavelength above 900 cm⁻¹, the results were displayed after 950 cm⁻¹. The analyses by FTIR enabled us to identify the change in chemical species before and after decomposition, thereby evaluating the interaction between the fuel component and HAN.

ASSOCIATED CONTENT

 Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c01804.

Mass change percentage of SS—Pt electrodes in repeated trials; temperature and current profiles of repeated trials using SS—Pt electrodes (PDF)

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NOTES

The authors declare no competing financial interest.

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