

Pyroelectric combustion rate characterization of electrically controlled solid propellants

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1 Introduction

Recent developments in solid rocket propellants have led to their inclusion in various propulsion systems. However, it necessitates to have control over combustion rates of such propellants in order to fulfill different mission requirements. Specifically, it is highly desirable when propellants can exhibit multiple cycles of start/stop capabilities during in-flight operations of a solid rocket motor. Electrically controlled solid propellants (ECSPs) are one such class that demonstrate this feature. These propellants ignite and combust when external electric power is applied at sufficient levels [1]. This process is highly exothermic and the combustion rate of these propellants can be controlled/adjusted by varying the applied power. Combustion extinguishes when the external power is removed, which can be restarted by reapplying the voltage and current to the propellant [2, 3]. This characteristic is known as the pyroelectric behaviour. In addition, ECSPs exhibit high stability and controllable throttle, and are not susceptible to accidental ignition by spark, impact or open flame.

Many studies on ECSPs based on hydroxyl ammonium nitrate (HAN) oxidizer have been reported in the past [3-6]. He et al. [4] have studied the thermal characteristics of different HAN-based ECSPs and showed their decomposition temperature ranges. Recently, Glascock et al. [5] have analyzed the ablation characteristics, impulse and performance measurements of such ECSPs within an arc discharge. Bao et al. [6] have studied the ignition and combustion behaviour of ECSPs containing aluminium (Al) as metal additive, and have proposed possible governing combustion mechanisms. However, HAN is highly hygroscopic which results in poor thermal stability for these ECSPs and limit their applications.

Therefore, lithium perchlorate (LP) has been considered recently instead of HAN in ECSPs, with polyvinyl alcohol (PVA) binder, to improve their thermal stability. He et al. [7] have investigated thermal and combustion characteristics of LP/PVA-based aluminized ECSPs, and showed that their burning rates increased with increasing the electrical voltage and ambient pressure. Similarly, Wang et al. [8] have studied the thermal reactivity, decomposition and combustion performance of polyethylene oxide-polyacrylonitrile (PEO-PAN) based ion conductive energetic composites, as a replacement for HAN-based ECSPs. Still, there are only limited studies on LP-based ECSPs that were attempted to investigate the factors influencing their thermal and combustion behaviours. In addition, the thermal decomposition and pyroelectric combustion mechanisms of ECSPs are not completely understood. In the present study, tungsten (W) is considered as a metal additive to investigate the pyroelectric combustion behaviour of LP-based metallized ECSPs, in comparison to the non-metallized baseline

propellant. The pyroelectric combustion rates are obtained as a function of applied initial voltage for different propellants and their relationship is studied as well.

2 Experimental

ECSP samples consist of lithium perchlorate as oxidizer, polyvinyl alcohol as binder and fuel, tungsten ($1\ \mu\text{m}$) as metal fuel additive, boric acid (H_3BO_3) as cross-linking agent and glycerin as plasticizer. Initial formulations of non-metallized and metallized propellants prepared in this study are shown in Table 1. For both samples, the original weight ratio of LP and water was maintained as 1:1.85, to achieve complete solubility of LP in water. The non-metallized baseline formulation was labelled as ECSP and 5% W containing formulation as ECSP-M5. The weight percent of other ingredients and LP/water ratio were maintained the same for both propellants, except for the metal content. The procedure for propellant preparation was explained in detail in our previous work [9]. At room temperature, distilled water, LP and boric acid were added to a container and mixed in a planetary centrifugal mixer (Thinky ARE-310, Japan). Subsequently, PVA was added to this mixture, which was de-aerated to remove air bubbles. For metallized samples, tungsten was added before PVA. A highly viscous propellant slurry was obtained after mixing, and it was cured in a hot air oven at $40\ ^\circ\text{C}$ for 7 days, to obtain a rubbery solid material. The final water content in ECSPs was different from the initial formulation, because some amount of water had evaporated during the curing process.

Table 1: Non-metallized and metallized ECSP compositions considered in this study.

Sample	LP (%)	H ₂ O (%)	PVA (%)	H ₃ BO ₃ (%)	Glycerin (%)	W (%)
ECSP	29.47	54.53	10	2	4	-
ECSP-M5	27.72	51.28	10	2	4	5

Combustion photography technique was implemented to obtain pyroelectric burning rates of ECSPs, by utilizing a combustion test stand and regulated DC power supply (1 kV and 1 A). The schematic of the experimental setup is shown in Fig. 1. The applied input power was recorded by performing voltage and current measurements through voltage and current probes, respectively, using a two-channel digital oscilloscope (Tektronix, model TBS1052B-EDU, 50 MHz bandwidth, sampling rate of 1 GS/s). The voltage probe was from Hantek company (T3100 model, maximum input of 2000 V, 100 MHz bandwidth, attenuation of 100:1) and the current probe was from Tektronix company (A622 model, range of 50 mA to 100 A, 100 kHz bandwidth, output scale of 100 mV/A). The combustion test stand consists of a set of electrodes made up of molybdenum, support stands and connections for input power. The dimensions of electrodes were $10\ \text{mm} \times 20\ \text{mm} \times 5\ \text{mm}$. The propellant and electrodes were positioned in a vertical burning configuration such that the top electrode was positive, the bottom electrode was negative and the propellant was placed in between these electrodes. When the external power was applied, pyroelectric combustion occurs at the top positive electrode, which gets displaced in the vertical direction by its own weight due to propellant burning. This vertical displacement ensured that the top electrode was always in continuous contact with the propellant burning surface, which was essential for pyroelectric combustion to occur.

The above vertical configuration was utilized to obtain pyroelectric combustion rates of ECSPs at different initial voltages measured from the corresponding probe, under ambient temperature and pressure conditions. The initial voltage was varied in the range of 100-500 V, at an increment of 100 V. ECSPs were cut into samples with a cross section of $\sim 4\ \text{mm} \times 4\ \text{mm}$ and length of 6-8 mm. The pyroelectric combustion process was captured using a high-speed camera (Phantom V711, with resolution of $800 \times 600\ \text{pixels}^2$) fitted with a 105 mm Nikkor macro lens, at a framing rate of 100 fps

and exposure time of 3000 μs [10]. A custom MATLAB code was utilized to obtain pyroelectric combustion rates. In this study, the displacement points of the moving top electrode were actually considered for this measurement, since it was highly challenging to locate the exact burning surface of propellants, and presumed to be exactly the same as regression rate of ECSPs. All data points at each initial voltage were repeated at least once and an uncertainty of $\pm 3\%$ was calculated for this measurement.

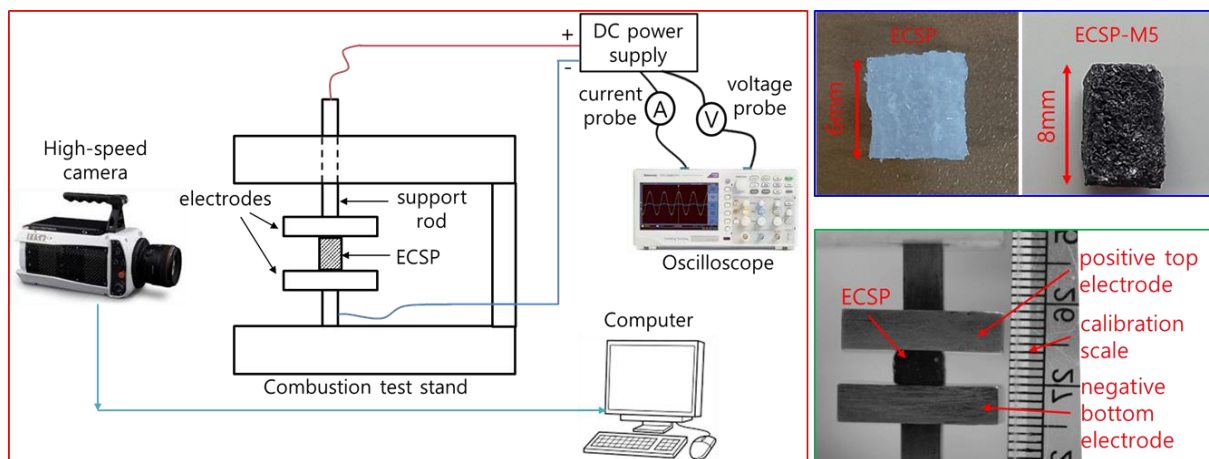


Figure 1: Schematic of the experimental setup (red box), images of ECSP and ECSP-M5 (blue box), and magnified view of the combustion test stand (green box).

3 Results

3.1 Pyroelectric combustion images

Combustion tests for non-metallized and metallized ECSPs were conducted at ambient conditions for different initial electrical powers, by varying the applied voltage in the range of 100 to 500 V and maintaining a constant current of 1 A in the external DC power source. When the external power source (set at 100V and 1 A) was turned on, the ECSP started to conduct the current from the top positive electrode to the bottom negative electrode. This initiated voltage and current values to increase progressively, as seen in the digital oscilloscope. At this stage, liquid bubbles were observed near the interface between the top electrode and propellant surface, which was caused by the evaporation of water still present in ECSPs. Once current and voltage reached their maximum values, ignition was achieved and pyroelectric combustion occurred at the top electrode-propellant burning surface. The combustion gases emerging out of the burning surface were restricted to flow upwards by the electrode itself, so these gases were forced out in the direction parallel to the interface. Since the top electrode was just placed on the flat propellant top surface and allowed to move freely in the vertical direction, it gradually displaced downwards at exactly the same rate as the propellant burning. Therefore, the rate of displacement of the top electrode was assumed as the pyroelectric combustion rate of these ECSPs. The pyroelectric combustion continued to occur as long as there was contact between the top electrode and the propellant burning surface. This process stopped when the contact was not present or when the propellant was completely consumed.

When the initial voltage was increased to higher values, the bubbling period due to water evaporation was decreased and the pyroelectric combustion of ECSP occurred at faster rates. This implies that high input power applied to ECSP improved their combustion rates. Similar observations were noticed with 5% metallized formulation (ECSP-M5), which exhibited slightly faster burning compared the non-metallized ECSP, at each initial voltage. Pyroelectric combustion images for ECSP and ECSP-M5 were obtained from high-speed imaging, and their corresponding instantaneous snapshots are shown in Fig. 2, for 400 V and 1 A at different time instances. Here, the first part in each image (Figs. 2a and 2b)

represents the occurrence of ignition (t_0), and further parts illustrate the pyroelectric combustion of ECSPs until they burn out completely. ECSPs are marked as red dotted boxes, and the top face of positive electrode and the bottom face of negative electrode are marked with green dotted lines. These figures clearly show the pyroelectric burning process and combustion gases being forced out in all directions near the top electrode, as mentioned above.

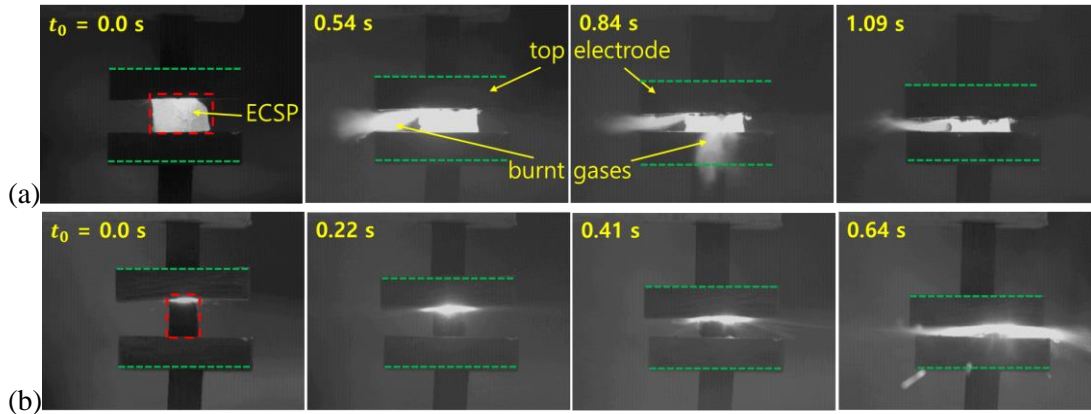


Figure 2: Instantaneous snapshots of pyroelectric combustion at 400 V and 1 A. (a) non-metallized ECSP and (b) 5% metallized ECSP-M5.

The top electrode (top green line) displaced regressively (by its own weight) along with the propellant burning surface to ensure continuous contact between themselves. Highly bright regions were noticed within the ECSP because the propellant grain was still translucent after curing, which allowed for transmission of the light radiation from the flame through the propellant. However, ECSP-M5 appeared dark within itself, while the combustion zone was much brighter than ECSP near the top electrode-propellant interface. This is attributed to the high energy release from combustion of tungsten particles in the metallized propellant. At an applied initial voltage of 400 V, pyroelectric combustion of ECSP and ECSP-M5 occurred over a period of 1.17 s and 0.90 s, respectively. This implies that the metallized ECSPs have burned slightly faster than non-metallized ECSPs, since the combustion time for the former was less than the latter. These combustion rate results will be discussed next.

3.2 Pyroelectric combustion rates

The change in voltage and current signals recorded during combustion tests of ECSP and ECSP-M5 at 400 V and 1 A are shown in Figs. 3(a) and 3(b), respectively. These data correspond to the combustion images shown in Fig. 2 in the above subsection. Both propellants followed a similar trend during the initial stage of pyroelectric combustion of ECSPs. The voltage started to rise gradually and attained a maximum of 400 V at the ignition point. On the other hand, the current reached a maximum of 1 A and then a minimum ~ 0.5 A before the ignition. During pyroelectric combustion, the voltage decreased slightly from 400 V to 300 V for ECSP and from 400 V to 325 V for ECSP-M5, respectively. However, the current signal fluctuated highly at ~ 1 A for both propellants in this time interval. Once the contact between the propellant and electrodes was lost, the voltage value dropped down to minimum and the combustion process was completed.

The time taken to attain maximum voltage (ignition) from the onset of voltage rise is termed as the voltage rise time in the present study. Fig. 3 illustrates that the voltage rise time for ECSP-M5 (0.36 s) was slightly lower than that of ECSP (0.54 s). This implies that the ionic conductivity of the former was higher than the latter, due to the presence of W particles that generally have high electrical conductivity. A previous study has reported that higher ionic conductivity for energetic materials indicate lower impedance, which causes such materials to be sensitive to voltage and reduces their response time when a voltage is applied [8]. This response time is considered analogous to the voltage rise time in the present

study. In addition, the overall combustion time of metallized propellant (0.8 s) was marginally less than the non-metallized case (1.1 s), similar to that in combustion snapshots shown earlier (Fig. 2).

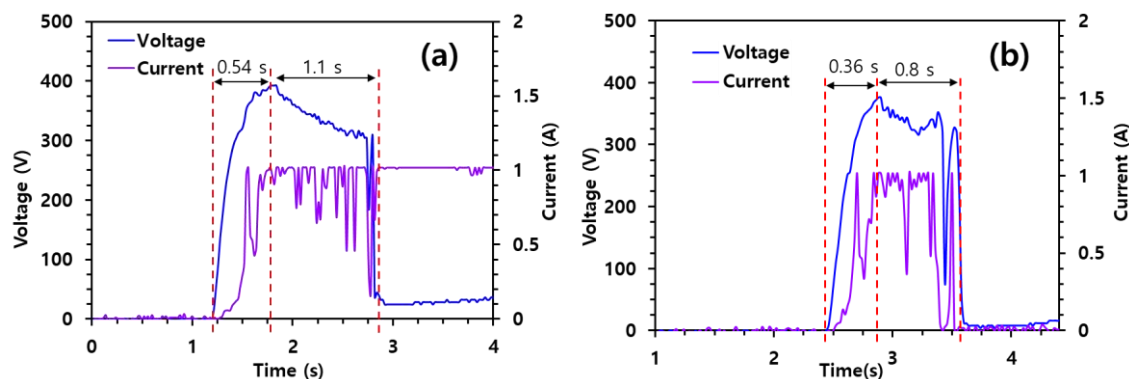


Figure 3: Voltage and current signals during pyroelectric combustion of (a) ECSP and (b) ECSP-M5 samples at 400V and 1 A.

The combustion images captured from high-speed imaging were utilized to obtain the pyroelectric combustion rates of ECSP samples, which are shown in Fig. 4 as a function of applied initial voltage. A pyroelectric combustion rate of ~ 0.3 mm/s was noticed for non-metallized ECSP at 100 V, which increased to ~ 3.0 mm/s at 500 V. In the considered voltage range, combustion rates have increased by 10 times for this sample, and an exponential trendline fit indicated a correlation of 80%. When tungsten was added to the ECSP formulation, combustion rates were obtained as ~ 0.50 mm/s at 100 V and ~ 3.0 mm/s at 500 V, respectively. An increment of 6 times in the combustion rate within this range and a correlation of 71% were observed with metallized ECSP-M5. Overall the trend for both ECSP and ECSP-M5 remained the same, with pyroelectric combustion rates increasing with increase in the initial voltage. This increasing trend is similar to results of linear burning rates vs. voltage reported by He et al. [7], for aluminized ECSPs ($\text{LiClO}_4/\text{PVA}/\text{Al}/\text{H}_2\text{O}$ propellants) in the range of 80-400 V dc.

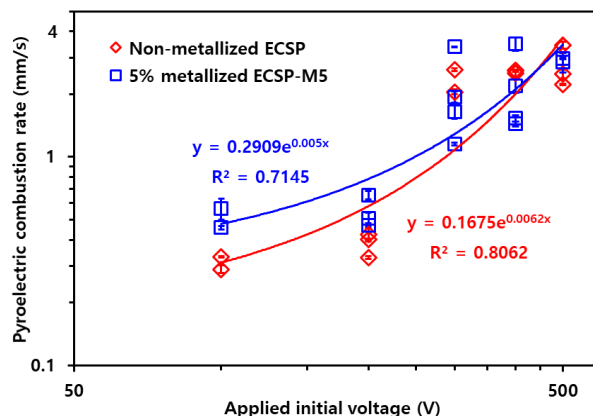


Figure 4: Pyroelectric combustion rates as a function of initial voltage for ECSP and ECSP-M5 samples.

Addition of W to ECSPs enhanced their pyroelectric combustion rates significantly only at low voltages (< 200 V), while this effect was negligible at high voltages (> 300 V). An increase of 66% in the combustion rate was noticed at 100 V for ECSP-M5 compared to ECSP, whereas it remained the same for both propellants at 500 V. This is seen as converging trendlines above 400 V (Fig. 4). Note that pyroelectric combustion of ECSPs is complex and involves electro-chemical mechanisms coupled with thermo-chemical reactions. The former is due to the electrolytic decomposition of ionic oxidizer (LP) at electrodes and the latter is caused by chemical reactions between different species, all resulting in

generation of heat to further sustain their corresponding processes. The trend observed in this study at high electrical power indicates that electro-chemical mechanisms were more dominant than thermo-chemical mechanisms in governing the pyroelectric combustion behaviour of ECSPs, regardless of the presence of metallic additives in the propellant formulation.

4 Conclusions

In this study, pyroelectric combustion rates of non-metallized and metallized electrically controlled solid propellants (ECSPs) were obtained as a function of different initial voltages and a comparison was presented. High-speed images of pyroelectric combustion of ECSPs showed that this process involved liquid bubbling, ignition at maximum voltage and current, followed by actual combustion at decreasing voltage and fluctuating current. Inclusion of tungsten (W) to ECSPs enhanced this process resulting in more luminous flame and decreased overall combustion time, relative to the non-metallized propellant. The voltage rise time or response time for ECSP-M5 was slightly lower than ECSP, implying that the presence of W increased the ionic conductivity of the former. Pyroelectric combustion rates of both ECSPs increased with the initial voltage and followed an exponential trend in the range of 100-500 V. However, ECSP-M5 showed 66% increment in the combustion rate relative to ECSP at 100 V, while it remained the same at 500 V between these propellants. This was due to dominant electro-chemical mechanisms that governed the combustion behaviour of ECSPs at high electrical power.

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