Communication

Electrochemical Modulation of the Flammability of Ionic Liquid Fuels

Prithwish Biswas, Yujie Wang, Erik Hagen, and Michael R. Zachariah*

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ABSTRACT: Flammability and combustion of high energy density liquid propellants are controlled by their volatility. We demonstrate a new concept through which the volatility of a high energy density ionic liquid propellant can be dynamically manipulated enabling one to (a) store a thermally insensitive oxidation resistant nonflammable fuel, (b) generate flammable vapor phase species electrochemically by applying a direct-current voltage bias, and (c) extinguish its flame by removing the voltage bias, which stops its volatilization. We show that a thermally stable imidazolium-based energy dense ionic liquid can be made flammable or nonflammable simply by application or withdrawal of a direct-current bias. This cycle can be repeated as often as desired. The estimated energy penalty of the electrochemical activation process is only ∼4% of the total energy release. This approach presents a paradigm shift, offering the potential to make a "safe fuel" or alternatively a simple electrochemically driven fuel metering scheme.

Storage and transportation of all conventionally used high energy density fuels have the potential to cause unintended fire and explosion.[1,2] Liquid hydrocarbons which are typically used as fuels combust in the vapor phase, and the heat feedback from the flame is able to vaporize enough fuel to self-sustain the combustion.[3−8] Therefore, the typical way to extinguish a flame is to remove the oxygen source (air) from the flame front. Alternatively, room temperature ionic liquids (RTIL) are a special class of hydrocarbons having extremely low vapor pressures, which on thermal decomposition produces oxidation resistant species.[9−13] Owing to these characteristics, RTILs are usually nonflammable and are often used as flame-retardant components in various materials for energy storage and conversion.[14−17]

However, RTILs also possess high energy densities which make them attractive fuel candidates for propulsion.[18] Energetic ionic liquids consisting of metastable anions such as azide, dinitramide, borohydride, and azole-based anions are known to thermally decompose to reactive flammable species.[19−23] This has led to the use of such RTILs as fuel components in propellant and explosive formulations. Additionally, thermally insensitive RTILs which are devoid of such reactive anions can also be chemically activated with white fuming nitric acid. When brought in contact with the acid, the RTILs are spontaneously oxidized, resulting in hypergolic ignition.[18,24] Termination of such a combustion process is difficult as it requires the segregation of the fuel and oxidizer.

In contrast, suppose one could dynamically manipulate the volatility of a nominally volatile and thermally stable RTIL, then in principle it should be possible to (a) store an involatile energetic liquid as nonflammable fuel, (b) make it flammable by increasing its volatility, and (c) extinguish its flame by decreasing its volatility. Realization of this approach will offer the potential to make a "safe fuel" or alternatively lay the foundation of a simple fuel metering scheme, which has never

been realized before in the domain of condensed phase propellants.

Herein, we show that the aromaticity of the imidazole ring, which makes the imidazolium based RTILs thermally stable and oxidation resistant,[25−27] can be broken electrochemically, resulting in the volatilization of the RTIL as flammable reactive species, which can ignite and generate a self-sustaining flame. Additionally, we demonstrate that the removal of the applied voltage bias terminates the electrochemical reactions, thereby stopping the volatilization of the RTIL resulting in the extinction of the flame. This facile strategy can be employed to control the energy generation from high energy density propellants. Such control on the energy release from condensed phase propellants,[28−33] enabling on-demand extinction of the flame, has not been demonstrated earlier to the best of our knowledge.

The concept of flammability switching is illustrated in Figure 1. As mentioned earlier nonflammable imidazolium RTILs are resistant to thermal shock and oxidation. However, when a voltage is applied across the RTIL, electrolysis of the RTIL results in its volatilization into flammable gas phase species, which can spontaneously ignite and combust. Continuous application of the voltage ensures continuous supply of reactive volatile fuel fragments to the flame, thereby leading to self-sustaining combustion. Withdrawing the voltage stops the volatilization of the RTIL, terminating the supply of the flammable species from the liquid phase to the flame, thereby leading to the extinction of the flame. As the RTIL is thermally
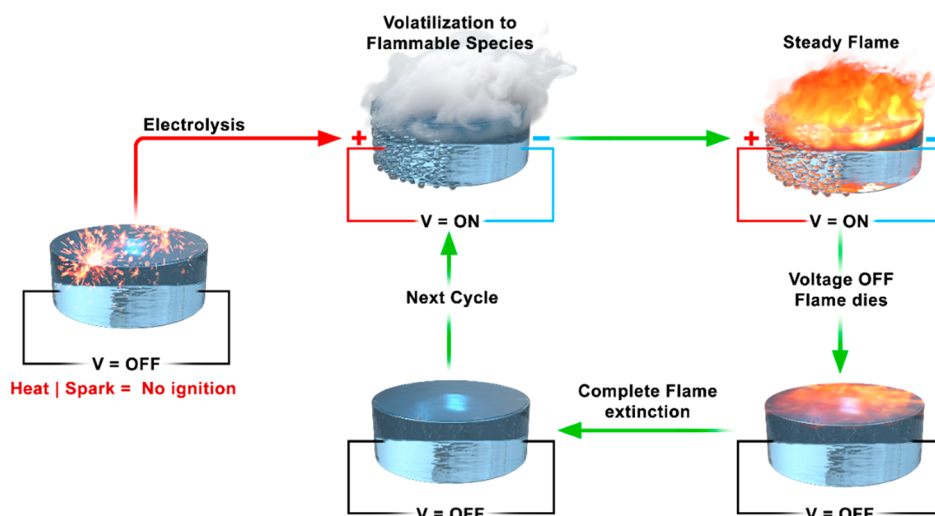
Figure 1. Concept of switching the flammability of RTILs via electrolysis. Imidazolium based RTILs are inherently insensitive to thermal shock/spark; however, they can be electrochemically volatilized to reactive flammable species, which can ignite and self-sustain a flame. Turning off the voltage terminates volatilization of the RTIL, thereby extinguishing the flame. This process can be repeated several times to sequentially meter the energy from the RTIL.
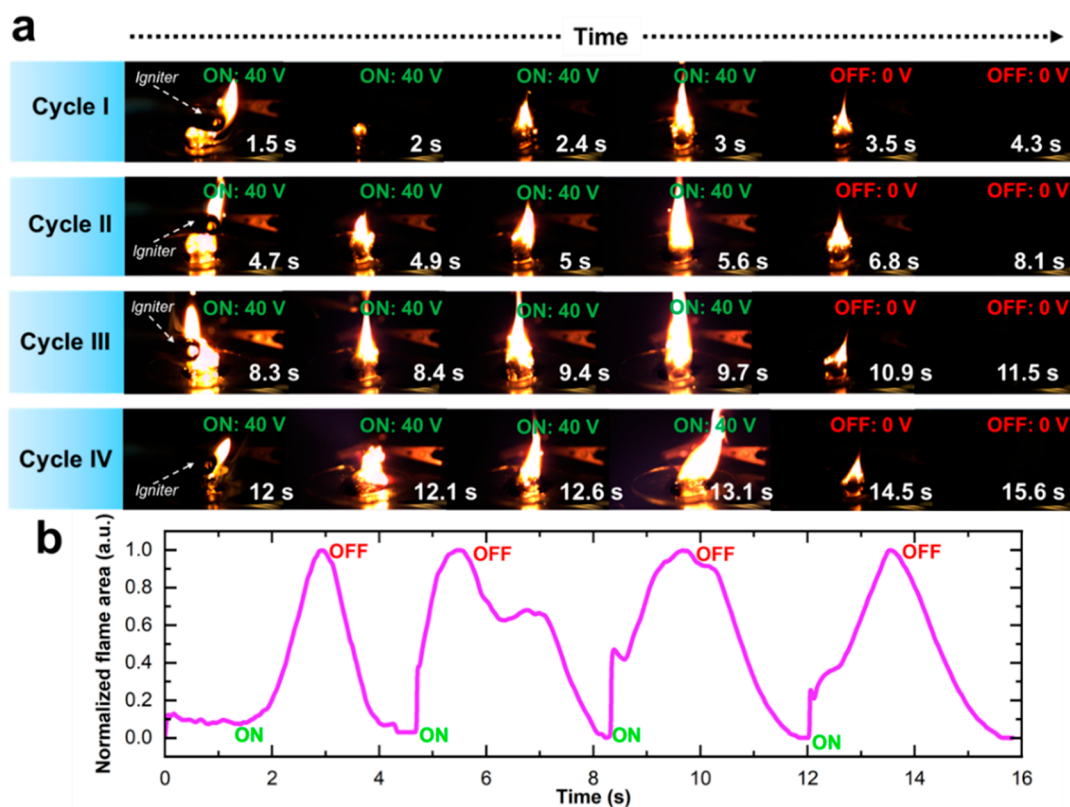

Figure 2. (a) High-speed camera imaging of the electrochemical activation and deactivation of the combustion process of RTIL to demonstrate the concept presented in Figure 1. (b) Flame area as a function of time from the high-speed camera imaging.

insensitive, the heat feedback from the flame is not able to generate significant vapor pressure or flammable gas phase species from the fuel. Hence, it can only ignite the flammable vapor phase species generated electrochemically and is unable to ignite the liquid RTIL. Leveraging this property, the vaporization and hence the flammability of the RTIL can be completely switched off by deactivating the electrochemical reactions through withdrawal of the voltage. Hence, we

demonstrated that the flammability of the RTIL can be completely reversed at will, by electrochemical means.

We have used 1-butyl 3-methyl imidazolium perchlorate ($[BMIM]^+[ClO_4]^-$) as a model imidazolium based RTIL for this specific demonstration. $[BMIM]^+[ClO_4]^-$ has been synthesized by the hard acid soft base anion exchange method by reacting dissolved precursors $[BMIM]^+[Cl]^-$ and $NaClO_4$. More details on the synthesis procedure and characterization can be found in section S.1, Figures S1 and S2 in the
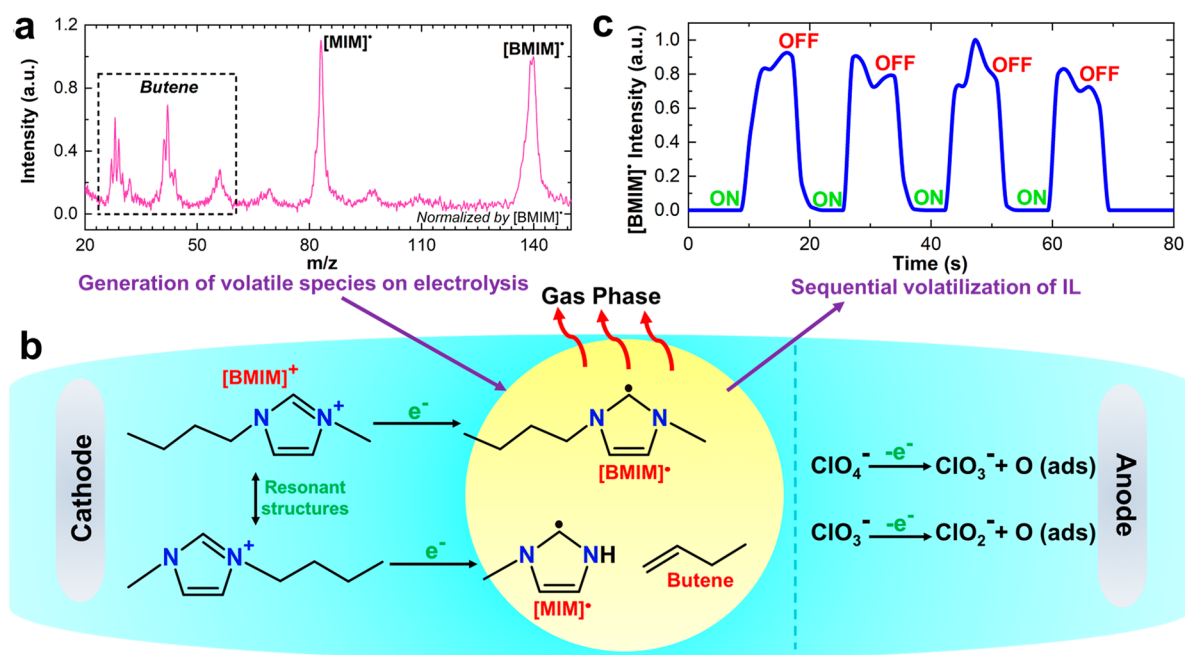
Figure 3. (a) Time-averaged electrochemical TOFMS spectra of $[BMIM]^+[ClO_4]^-$ showing the evolution of volatile species from the RTIL. (b) Electrochemical reduction mechanism of $[BMIM]^+$ to gas phase $[BMIM]^\bullet$ and $[MIM]^\bullet$. (c) Sequential volatilization of $[BMIM]^+[ClO_4]^-$ as inflammable $[BMIM]^\bullet$.

Supporting Information. Prior studies have reported that, on thermal decomposition, the imidazolium ion forms 1-methylimidazole in the vapor phase and imidazole oligomers in the liquid phase.[34,35] Therefore, the oxidation resistant aromatic imidazole ring remains intact in both phases, which makes the RTIL nonflammable. Thermogravimetric analysis coupled with differential scanning calorimetry (TGA/DSC) measurements show that $[BMIM]^+[ClO_4]^-$ exothermically loses 80% of its mass between ~523 and 610 K (Figure S3), which can be attributed to the generation of vapor phase imidazoles.[36] Although this RTIL undergoes exothermic thermal decomposition, we demonstrate that it cannot be ignited thermally by hot-wire ignition at high heating rates (Figure S4) or by contacting a butane flame (Figure S5), thereby proving that it is resistant to thermochemically driven oxidation.

However, as mentioned earlier, the combustion event of $[BMIM]^+[ClO_4]^-$ can be electrochemically activated/deactivated in multiple cycles, as demonstrated in Figure 2. For performing the demonstration, $[BMIM]^+[ClO_4]^-$ liquid was electrochemically activated with two Pt wire electrodes (~75 μm diameter), as shown in the representative schematic (Figure 1). When the voltage ($V = 40$ V) is applied, in the absence of an external igniter, smoke and gas bubbles are generated only at the cathode as observed by high-speed optical and IR imaging (Figure S6). Figure 2 a and video SV1 show that when a butane flame is held above the surface of the RTIL after turning on the voltage, the gaseous species released can be ignited. The flame height gradually grows and becomes constant indicating the ability of the gaseous species generated on electrolysis to undergo self-sustaining combustion. When the voltage is turned off, the flame height decreases and the flame is extinguished as the generation and supply of volatile flammable species to the flame is inhibited. The flame area from these images have been estimated by counting the number of bright pixels after excluding the frames containing

the butane flame, and the time-evolution of the normalized flame area has been represented in Figure 2b after moving-average smoothing, to corroborate the visual observations presented in Figure 2a. This clearly demonstrates the aforementioned concept of controlling the thermal energy generation from RTILs, by sequentially dispensing and combusting volatile species from the condensed phase RTIL, which remains unaffected by the heat feedback from the flame. We used a voltage of 40 V for the demonstration purpose. Considering the electrochemical stability window of the RTILs[37,38] from voltametric measurements, any applied voltage above ~6 V will be able to electrolyze the given RTIL.[39] The effect of the voltage on the ignition delay should be addressed in future studies.

The model RTIL, $[BMIM]^+[ClO_4]^-$, has been electrolyzed under vacuum, and the evolving vapor and gas phase species have been directly sampled and analyzed by time-of-flight mass spectrometry[40] as explained in the methods section (section S.1). The time-averaged mass spectra (Figure 3a) collected over ~100 ms by sampling at an interval of ~0.1 ms shows the generation of 1-methyl 3-butyl imidazole-2-yl radical ($[BMIM]^\bullet$, $m/z = 139$), 1-methyl imidazole-2-yl radical ($[MIM]^\bullet$, $m/z = 83$), and butene ($m/z = 28, 41, 56$).[41]

The generation of these radicals can be explained by the cathodic reduction of the BMIM cation, as shown in Figure 3b. On gaining an electron, the isomer of the BMIM cation having a methyl group attached to the N^+ forms $[BMIM]^\bullet$ whereas the other isomer with the butyl group attached to the N^+ results in the formation of $[MIM]^\bullet$ and butene. In order to verify this mechanism, we also characterized other commercially available RTILs such as $[BMIM]^+[PF_6]^-$ and $[EMIM]^+[BF_4]^-$. The $[BMIM]^+[PF_6]^-$ shows both $[BMIM]^\bullet$ and $[MIM]^\bullet$ peaks (Figure S7), as observed in the case of $[BMIM]^+[ClO_4]^-$, indicating that the cathodic reaction of the BMIM-cation is independent of the anion attached to it. The $[EMIM]^+[BF_4]^-$ also shows $[EMIM]^\bullet$ and $[MIM]^\bullet$ peaks

(Figure S7), indicating that the formation of imidazole-2-yl radicals by cathodic reduction is independent of the alkyl chain length attached to the N^+ of the BMIM-cation. This shows that the electrochemical reduction mechanism shown in Figure 3b can be generically applied to all imidazolium-based cations. The existence and the stability of these radicals have been also reported in previous studies.[42−45] The absence of vapor phase species from the anodic reaction indicates the $[ClO_4]^-$ has undergone partial oxidation to chlorate ($[ClO_3]^-$) and chlorite ($[ClO_2]^-$) ions,[46−48] as its complete transformation to gas phase chlorine and oxygen requires multiple electron transfers, which is highly unlikely in the absence of an electro-catalyst. This is also supported by the fact that BF_3 and PF_5 gases appear in the obtained mass spectra of $[EMIM]^+[BF_4]^-$ and $[BMIM]^+[PF_6]^-$ respectively (Figure S7), from one-electron oxidation of the respective anions.

Thus, electrochemical reduction breaks the aromaticity of the imidazole ring, thereby generating gas phase $[BMIM]^•$, $[MIM]^•$, and butene. As the aromaticity of the imidazole ring significantly limits the flammability of the RTIL,[25,26] its absence makes the generated gas phase species prone to oxidation and hence these evolved species are highly flammable. Additionally, as shown in Figure 3c, it is possible to sequentially dispense $[BMIM]^•$ by turning on/off the external voltage periodically. The volatility of $[MIM]^•$ (Figure S8) can also be manipulated in the same manner as that of $[BMIM]^•$ by periodically controlling the external voltage. This corroborates the temporal variation of the flame area on application and withdrawal of the direct-current bias (Figure 2). This indicates that the application of the direct-current bias on the RTIL generates volatile flammable species such as $[BMIM]^•$, $[MIM]^•$, and butene leading to a self-sustained flame, whereas an open circuit stops the volatilization of the RTIL into these species, thereby extinguishing the flame.

In summary, we have demonstrated for the first time that the flammability of a thermally insensitive, oxidation resistant liquid fuel can be reversed simply by applying and withdrawing a voltage across it. Therefore, this approach does not require any separation of fuel from the oxidizer to manipulate flammability. In the current study, we have demonstrated this effect by using a nonflammable model imidazolium based room temperature ionic liquid (RTIL). The aromaticity of the imidazole ring makes the RTIL resistant to thermal shock and oxidation. We show that the aromaticity can be broken by electrochemical reduction of the imidazolium ion, which results in its gasification, and the evolved gases being more prone to oxidation can be ignited and combusted. Removal of the voltage shuts off the electrochemical reduction process, thereby cutting off the supply of volatile flammable species to the flame, resulting in its complete extinction. Theoretically, the complete combustion of imidazolium ionic liquids can potentially generate ∼20 kJ/g according to the calculation shown in S.2, whereas the work performed to electrolyze the liquid is ∼0.8 kJ/g; that is, the energy penalty associated with the electrolysis process is only 4%. Thus, these findings may bring in a paradigm shift by enabling the use of RTILs as safe energy-dense fuels, the energy generation from which can be controlled in a sequential manner. Moreover, this study lays the foundation of several fundamental studies that will focus on evaluation of the major degrees of freedom controlling the thermal energy release profile of these systems along with the characterization of their flame temperature and energy release rates.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.3c04820.

> Detailed experimental methods, supporting characterizations based on FTIR, TGA/DSC, XRD, IR thermometry, *in situ* mass spectrometry of different RTILs, hot wire ignition, and combustion enthalpy calculation. (PDF)

> Video SV1: Ignition of flammable gas phase species after application of voltage to RTIL. (MP4)

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Notes

The authors declare no competing financial interest.

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