Alkali Metal Based Micro Combustion Using Graphene Micro-valve Trigger

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Abstract. Controllable combustion of alkali metals offers a pathway to high energy density, high power density scalable thermal systems. The volatile nature of these materials however, has limited their incorporation into useable devices. Recent findings in low trigger power MEMS one-shot valves offer a viable pathway forward for creating systems in which to exploit the unique properties of alkali metals as thermal energy sources. By miniaturizing and combining these fuels with such a valve, and incorporating them with a polymer substrate, a micro-packet of combustible metal can be created. Here we report such a device utilizing a graphene based micro-valve trigger and a rubidium metal fuel source to realize an arrayable micro-scale electrical to thermal energy amplification scheme. Using this approach we can react nanoliter droplets of rubidium with ambient air on demand, producing electrical to thermal energy gains of seventy five times. By arraying the fuel into discrete packets, we can also achieve temporal control of the fuel source, allowing for tailored peak and average power output.

1. Introduction
Alkali metals are an energy dense fuel source that inherently have high power density due to their low ionization energy and thus high reactivity. This makes these elements particularly interesting for energy applications. Their reactivity, however, makes the processing, storage and actuation of these fuels in a controlled manner difficult. As a result, the properties of these materials are not typically exploited.

Recent advances in MEMS one-shot valves have offered a pathway forward for integrated alkali metal systems by providing low input-power actuation sources with a leak-free seal [1]. These valves provide oxidation free storage for containment and are a perfect trigger mechanism for actuating fuels utilizing ambient oxygen for combustion. Our approach employs such a device as a key portion of a novel, arrayable and scalable integrated thermal power generation system employing alkali metal fuel, micro-valve and a polymer layer acting as a seal and characterization mechanism.

2. Device Concept
Due to the reactive nature of the proposed fuels, temporal control of the fuel reaction is imperative for exploitation of the unique properties of these materials. In order to solve this issue, we divide the fuel into tiny packets that are placed into the micro-valve and can be triggered on demand to tailor peak and average power output. The basic cell of our device is comprised of three parts: a rubidium droplet (the
fuel) contained within a graphene micro-valve (the trigger/barrier) sealed with a polymer film on the backside (structural layer/seal) bonded by heating. Figure 1 shows the assembly and overlying structure of such a device. The operation of the device begins with a current pulse, which fractures the graphene valve and allows ambient air to react with the rubidium. The heat generated by this reaction vaporizes the underlying polymer, which provides a mechanism for quantifying the amount of heat generated. Figure 2 gives a theoretical analysis of the energy delivered or required for each system component as a function of cell dimension.

3. Alkali Fuel Source

Alkali metal fuel sources offer the potential for extremely high specific power densities under oxidation, while maintaining excellent energy densities. For this device, we focused on rubidium as our fuel as volumetric energy density and reactivity of the alkali metals generally increases with increasing period. Furthermore, rubidium is pyrophoric and spontaneously ignites in air, a behavior which lower period alkalis do not possess, making an ignition source unnecessary.

When Rb fuel is allowed to spontaneously ignite in air, it has a specific power density of about 2 MW/kg, dwarfing conventional supercapacitors (around 15 kW/kg) by about two orders of magnitude [2]. Its energy density of about 550 W-hr/kg beats current lithium ion technology, winning by 2-5 times [3]. However, the fact that these fuels rely on spontaneous chemical reactions means that power delivery lasts only about one second, making long-term applications difficult. Figure 3 shows the short timescale energy release of a 100 μL Rb droplet.

![Figure 1. Fabrication schematic of micro-valve alkali metal cell for energy conversion.](image)

![Figure 2. Energy requirement or delivery for each part of the system. Polymer thickness taken to be 10% of micro-packet dimension. Delivered energy far outweighs the energy input requirement. For a detailed analysis of the valve energy see [1]. Polymer energy is calculated from a molar heat of vaporization of 110 kJ/mol and heat capacity of 1.2 J/g-K. Rubidium energy is calculated from the enthalpy of formation of Rb₂O (-169.5 kJ/mol, worst case scenario).](image)

![Figure 3. Top: IR images separated by 0.3s showing before (left) and after (right) auto-ignition of Rb. Bottom: Corresponding IR data for a point on the Rb surface. We see ignition timescales on the order of 0.5-1.0 s for droplets 100 nL – 100 μL.](image)
4. Graphene Micro-valve Trigger
Rubidium needs to be packaged and remain in inert atmosphere until triggered and exposed to ambient air. Our triggering approach follows previously reported work on graphene-based one-shot micro-valves [1] that use significantly low input electrical energy for thermo-mechanical cleaving. We have shown 100% reliability for triggered actuation of >100 valves. Valves were fabricated in the same method as previously reported, producing valves 750 x 750 μm having approximately 360 nm thick silicon nitride membranes with Ni electrodes and patterned graphene. These valves have been shown to be leak-free and the fabrication processes for these devices allows for extensive variation, enabling scaling of valve size and density for tailoring of application. Figure 4 shows a valve before and after valve triggering.

5. Polymer Based Substrate and Characterization Platform
On the backside of the valve we utilize a blended polycarbonate polymer to realize both mechanical rigidity for use as a backing layer as well as low vaporization temperature for power generation characterization. The polymer also acts as the backside seal for the device, allowing for the fuel to be protected from ambient air until triggered via graphene valve.

The blended polycarbonate used in this study was a 30/70 blend of a vaporizable polycarbonate (VPC) synthesised based on [4] and commercially available polypropylene carbonate (PPC). This VPC offers low vaporization temperature but is limited to thin spin coated films [5]. Blending the VPC with commercial PPC allows for thick films approximately 125 μm thick to be drop cast which can act as packaging to our system while still having excellent decomposition properties.

Furthermore, the vaporizable nature of our polymer allows for characterization of our thermal energy release system. When actuated, the heat produced by the fuel will vaporize the polymer substrate. Through optical microscopy and profilometry we can determine the amount of removed polymer. Combining this with the decomposition properties of the polymer obtained using commercial thermogravimetric analysis, we have a means of quantifying energy release on the small scale of our devices. Our blended polymer typically show a decomposition temperature of ~ 180 °C.

6. Device Assembly
All assembly takes place in an inert atmosphere devoid of oxygen (argon glove box with O₂ concentration < 1 ppm). Rubidium (99.75% metals basis) is stored under mineral oil until deposited. Deposition was accomplished by heating the Rb in oil to above the melting temperature and transferred via a resistively heated zero-dead volume syringe. Volumes of Rb droplets ranging from tens of nL to hundreds of μL can be prepared in this manner.

Rb droplets were transferred to polymer substrates in this manner. The graphene valve is then placed over the droplet and the whole system moved to a hot plate heated to below, but near the polymer glass transition temperature (typically 70 °C). This softens the polymer enough to adhere the MEMS valve to the surface in order to seal the system. A silicon spacer is used to prevent the polymer from sticking to the hot plate. Once sealed, the devices are placed in sealed containers and transferred from the glovebox for testing. The devices remain under argon until wire bonding and subsequent actuation.

7. Device Testing
Tested devices were 750x750 μm and consume 140 mW for about 14 ms before triggering. These can fit 500 nL of Rb, which can release up to 1.53 J upon oxidation. This implies a theoretical maximum
energy gain of nearly 800 times. Figure 5 shows the waveform used to trigger the valve and corresponding temperature increase as seen from the backside of the polymer via IR camera. Tested devices, shown in Figure 6, demonstrate polymer etching. These devices were heated to 65 °C before triggering in order to melt the Rb and aid in spontaneous ignition. This higher than ambient initial temperature was accounted for in calculation. Calculations show up to 9.6% of the theoretical Rb energy is transferred to the polymer, corresponding to 75x electrical to thermal energy gain. This demonstrates successful sealing, actuation and heat generation of our proposed device. Loss mechanisms to the air and valve structure are significant, and future experimentation will focus on removing these loss mechanisms by creating a fully polymer system.

8. Conclusions
While successful storage and actuation of rubidium fuel has been demonstrated, we foresee various improvements and advancements with the current system. Moving from rubidium to caesium is expected to increase power and energy density, while varying valve size and density will allow for on-demand control of energy and power output. Integration of thermoelectrics poses an interesting application for a low electrical energy input to high energy output system and finally, a fully polymer system could pave the way for total device transience and totally vanishing electronics.

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