

| | Lift-Gas Cracker | Electrolytic Generator |
|---|------------------|------------------------|
| Mass, kg | <100 | >2,000 |
| Area, m ² | <1 | >4 |
| Electrical Power, kW | <0.5 | ≈100 (From Generator) |
| Fuel, Grams per Standard Liter of Gas | 0.1 | 1.4 |
| Methanol, Grams per Standard Liter of Gas | 0.35 | 0 |
| Water, Grams per Standard Liter of Gas | 0.2 | 0.8 |
| Cost, Dollars (at 2003 Prices) | <\$10,000 | >\$50,000 |

Selected Parameters are presented in comparison of an LGC capable of generating hydrogen-based lift gas and an electrolytic apparatus capable of generating hydrogen — both at a rate of 100 standard liters per minute.

vantageous in several ways: As shown by example in the table, relative to an electrolytic apparatus capable of producing hydrogen at a given rate, an LGC capable of producing hydrogen-based lift gas at the same rate is much less massive and requires much less electrical power and

much less fuel. Moreover, the LGC is more reliable and robust.

As contemplated for use in extending the duration of flight of a high-altitude balloon, an LGC would provide the lift gas for an auxiliary buoyancy-control balloon separate from a main lift bal-

loon. The buoyancy-control balloon would be used to compensate for changes in buoyancy associated with diurnal/nocturnal variations in temperature. In this application, the LGC would produce the lift gas by catalytic reforming of methanol at night. During the day, some of the lift gas would be burned with atmospheric air to produce water for use as ballast. At night, the water ballast could be dropped or could be recycled to the LGC for steam reforming of methanol. In this approach, the duration of flight could be extended by a factor of as much as four, relative to a conventional approach in which ballast is dropped at night and gas is vented during the day.

This work was done by Robert Zubrin and Mark Berggren of Pioneer Astronautics for Goddard Space Flight Center. Further information is contained in a TSP (see page 1). GSC-14792-1

Ionic Liquids to Replace Hydrazine

Customized ionic liquids offer better safety and convenience than traditional propellants.

Dryden Flight Research Center, Edwards, California

A method for developing safe, easy-to-handle propellants has been developed based upon ionic liquids (ILs) or their eutectic mixtures. An IL is a binary combination of a typically organic cation and anion, which generally produces an ionic salt with a melting point below 100 °C. Many ILs have melting points near, or even below, room temperature (room temperature ionic liquids, RTILs). More importantly, a number of ILs have a positive enthalpy of formation. This means the thermal energy released during decomposition reactions makes energetic ILs ideal for use as propellants. Unlike traditional, storable propellants like hydrazine, ILs also exhibit near-zero vapor pressure. This makes them safer to handle because it eliminates hazardous inhalation — the primary pathway — as a route for toxicity in humans. Thus, ILs are ideal candidates for replacing hydrazine, which is expensive and dangerous, and poses significant handling difficulties.

Another behavior exhibited by ILs that makes them particularly attractive for replacing state-of-the-art, storable propellants is the very wide temperature range in which they remain liquid. A number of ILs have been routinely synthesized to possess glass transition points

below -60 °C (-76 °F), and decomposition temperatures in excess of 140 °C (284 °F). This behavior eliminates the stringent thermal control required for hydrazine, which freezes at 2 °C (35 °F) and boils at 113 °C (235 °F). If an IL-based propulsion system were used, spacecraft power otherwise needed to run heaters that keep hydrazine in a liquid state would be freed up for other power-hungry devices.

Another operations and safety benefit is that researchers have tremendous flexibility for dialing-in the precise behavior desired. The primary method for designing an IL for a specific task has been through careful selection of the two counterions — the cation and anion where each introduces specific properties to the binary, ionically bonded salt.

Scientists estimate there are as many as 10¹⁸ possible binary ILs, which gives considerable design freedom to researchers developing new propellants. This design trade space becomes significantly larger by using eutectic mixtures of ILs. Eutectic mixtures are important because they allow for precise tailoring of decomposition thermochemistry, fluid viscosity, melting point, glass transition point, density, and virtually every other physical attribute. Recently research was completed

that began to exploit eutectic mixture ILs specifically for tailoring their behavior to optimize their use as energetic monopropellants. The goal of that effort was to develop an IL monopropellant with higher Isp (specific impulse) performance than hydrazine.

In this specific work, to date, a baseline set of energetic ILs has been identified, synthesized, and characterized. Many of the ILs in this set have excellent performance potential in their own right. In all, ten ILs were characterized for their enthalpy of formation, density, melting point, glass transition point (if applicable), and decomposition temperature. Enthalpy of formation was measured using a microcalorimeter designed specifically to test milligram amounts of energetic materials. Of the ten ILs characterized, five offer higher Isp performance than hydrazine, ranging between 10 and 113 seconds higher than the state-of-the-art propellant. To achieve this level of performance, the energetic cations 4-amino-1,2,4-triazolium and 3-amino-1,2,4-triazolium were paired with various anions in the nitrate, dicyanamide, chloride, and 3-nitro-1,2,4-triazole families. Protonation, alkylation, and butylation synthesis routes were used for creation of the different salts.

With this baseline established, future efforts will examine a large number of eutectic mixtures of these various ILs. In particular, the dicyanamide-based ILs appear to offer high performance potential, while preserving the large liquidus range so desirable for propellants. Importantly, the dicyanamide ILs did not contain any oxidizing atoms (oxygen, chlorine, fluorine), which should further enhance operational safety.

One common complaint regarding IL propellants is their high viscosity. Scientists' ability to accurately predict, *a priori*, any fluid property of a binary IL — much less a eutectic mixture of two binary ILs — is still in its infancy. However, a trend that has been seen is that large structural differences between the cation and anion seem to improve fluid properties. Therefore, one goal for future efforts will be to experiment with

different IL cores and mixtures to maximize Isp performance and density, while simultaneously reducing liquid viscosity and glass transition point.

This work was done by Syri Koelfgen of Dryden Flight Research Center; Joe Sims, Melissa Forton, and Barry Allan of Analytical Services, Inc.; and Robin Rogers and Julia Shamshina of the University of Alabama. Further information is contained in a TSP (see page 1). DRC-010-041

Variable Emittance Electrochromics Using Ionic Electrolytes and Low Solar Absorptance Coatings

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One of the last remaining technical hurdles with variable emittance devices or skins based on conducting polymer electrochromics is the high solar absorptance of their top surfaces. This high solar absorptance causes overheating of the skin when facing the Sun in space. Existing technologies such as mechanical louvers or loop heat pipes are virtually inapplicable to micro (< 20 kg) and nano (< 5 kg) spacecraft.

Novel coatings lower the solar absorption to Alpha(s) of between 0.30 and

0.46. Coupled with the emittance properties of the variable emittance skins, this lowers the surface temperature of the skins facing the Sun to between 30 and 60 °C, which is much lower than previous results of 100 °C, and is well within acceptable satellite operations ranges. The performance of this technology is better than that of current new technologies such as microelectromechanical systems (MEMS), electrostatics, and electrophoretics, especially in applications involving micro and nano spacecraft.

The coatings are deposited inside a high vacuum, layering multiple coatings onto the top surfaces of variable emittance skins. They are completely transparent in the entire relevant infrared region (about 2 to 45 microns), but highly reflective in the visible-NIR (near infrared) region of relevance to solar absorptance.

This work was done by Prasanna Chandrasekhar of Ashwin-Ushas Corporation, Inc. for Goddard Space Flight Center. Further information is contained in a TSP (see page 1). GSC-15601-1