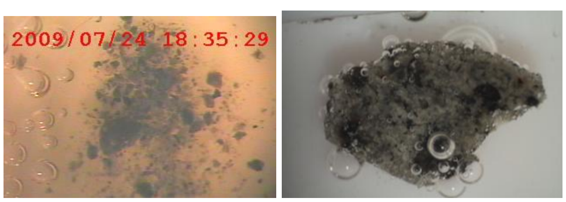
Task-Specific Ionic Liquids for Mars Exploration (Green Chemistry for a Red Planet). L. J. Karr[1], P.A Curreri[1], M.S. Paley[2], W.F. Kaukler[3] and M. J. Marone[4], [1]NASA/MSFC, Huntsville, AL 35812, [2]AZ Technology, 7047 Old Madison Pike, Suite 300, Huntsville, AL 35806, [3]University of Alabama in Huntsville, Huntsville, AL 35899. [4]Mercer University, Dept. of Physics, Macon, GA 31207.

Introduction: Ionic Liquids (ILs) are organic salts with low melting points that are liquid at or near room temperature. The combinations of available ions and task-specific molecular designability make them suitable for a huge variety of tasks. Because of their low flammability, low vapor pressure, and stability in harsh environments (extreme temperatures, hard vacuum) they are generally much safer and "greener" than conventional chemicals and are thus suitable for a wide range of applications that support NASA exploration goals. This presentation describes several of the ongoing applications that are being developed at MSFC.

***In Situ* Resource Utilization Applications:** The use of *in situ* materials and energy is essential for safe and economical sustained human presence beyond Low Earth Orbit. Precursor robotic missions will be necessary to determine what resources will be available and to demonstrate the capabilities for their use.

Oxygen and metal extraction from Martian Regolith. Recent efforts at MSFC have shown that acidic Ionic Liquids (ILs) can be used in a low temperature (< 200° C) process to solubilize regolith, and to extract as water up to 80% of the oxygen available in metal oxides. [1, 2] Using this method, we have solubilized lunar regolith simulant (JSC-1A), as well as extraterrestrial materials in the form of meteorites.



Lunar Meteorite (L) and Martian Meteorite (R) Dissolving in IL

Moreover, by using a hydrogen gas electrode, we have shown that the IL can be regenerated at the anode and metals (e.g. iron) can be plated onto the cathode. These attributes make ILs processing an excellent candidate for extracting oxygen *in situ*, for life support and propulsion, and for extracting metals to be used as feedstock in fabrication processes. (Current TRL: 4)

Efficient Electrochemical Reduction of Carbon Dioxide and Water to Hydrocarbons (Methane) MSFC and KSC (POC: Anthony Muscatello) are collaborating on a new start proposal to demonstrate the ability to produce propellants on the surface of Mars. This would entail a simple approach using task-specific ILs to capture CO_2 from the atmosphere, and in a single vessel, perform co-electrolysis of the CO_2 and martian H_20 in the IL to form methane. The Sebatier and Fischer-Tropsch processes are well known for chemical reduction of carbon dioxide to hydrocarbons using hydrogen as the reducing agent at elevated temperatures with specialized catalysts. However, the conversion efficiencies are limited and the catalysts are often vulnerable to becoming poisoned. In recent years, interest has grown in utilizing electrochemical means for carrying out CO_2 reduction in the presence of water utilizing ionic liquids (ILs) as electrolytes. ILs have long been known to be excellent media for both physical and chemical sorption of carbon dioxide; in the latter case efficiencies can reach the theoretical limit (one mol of CO_2 per mol of IL) [3, 4]. By exploiting recent developments in the chemistry and electrochemistry of CO_2 in ILs, we should be able to reduce CO_2 and water to fuels using ILs, with much improved efficiencies. This should reduce the cost, complexity and risk of Mars sample return and human Mars missions. (Current TRL: 2)

Chemical drill for analysis of regolith. Using the same acidic IL that is used for dissolving regolith simulant and meteorite material, MSFC has begun a project to demonstrate a drill that can go through Martian regolith with the aid of solubilization, and bring up samples in a liquid form that can be used for *in situ* analyses of chemical content. Drilling into a planetary body or asteroid is required for sampling the material beneath the surface for geological investigations, or to install sensors to monitor the planet's temperature or tremors over the long term, or to anchor a structure to withstand the wind on Mars surface. Since there is no requirement for speed or astronaut operation, one can save energy and up-mass by implementing a novel, autonomous drilling method that uses an ionic liquid to break up and partially dissolve the regolith at the tip of the drill. Mechanical drill performance would be greatly enhanced by injecting some ionic liquid to break up the regolith ahead of it. Power consumption would be greatly reduced and drills would not have to be frequently replaced. Alternatively, a purely chemical drill would use the ionic liquid to solublize the rocks and regolith and remove material in liquid form. A flexible plastic tube would deliver the IL to the bottom of the hole. One could even make a curved hole to better anchor a structure. As a serendipitous advantage, the sampled regolith solution carried to the surface is in a form that offers advantages in analytical instrument designs and opens possibilities for new wet chemical techniques for compound analysis (as opposed to elemental analysis). (Current TRL: 2/3)

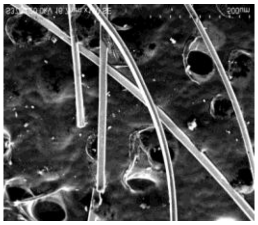
Ionic Liquids-Based Structural Application: Beyond *In Situ* Resource Utilization applications, research in Ionic Liquids at MSFC has focused on development of structural materials which NASA will need for exploration.

Composite Cryotanks. A unique Ionic Liquid epoxy (ILE) was developed at MSFC for which a U.S. patent has been applied for and approved. Mechanical and chemical testing has shown that this ILE monomer, when cured with a commercial aromatic diamine curing agent, yields polymer resin with high tensile strength, excellent bond strength to aluminum and steel, high toughness, low coefficient of thermal expansion (CTE) and low moisture permeability. Performance comparisons of the ILE to several commercial epoxies showed it had superior tensile and bond strengths. Of particular importance is that these properties of the ILE were even better at cryogenic temperatures. The IL epoxy was therefore expected to make an excellent matrix for a carbon fiber composite material such that it was the subject of a recent NASA SBIR.

Wound and cured IL epoxy/carbon composite

A number of preliminary tests of this composite material at 20° and -200° C showed that the ILE composite had a comparable CTE and tensile strength when compared to a commercially available carbon composite material, and had a much superior toughness. There was no microcracking under microscopic examination after repeated cryo-cycling . Composite fuel tanks can save 30% or more of the mass over a conventional alluminum alloy tank. This mass savings has not been realized even after decades of development due to microcracking after thermal cycling resulting in high permeability of the tank contents. The chemistry of this ILE composite leads us to expect it to have high resistance to chemical attack from candidate fuels such as liquid methane or nitrous oxide. (Current TRL: 4)

Ionic Liquid Process for Cellulosic Based Carbon Fiber (IL-CCF) Carbon fiber (CF) made from rayon precursor is a critical material to make carbon-carbon Solid Rocket Motors (SRM) and re-entry heat shields. The Air Force, Army and NASA share interest for rayon precursor CF to be used in missile and spacecraft TPS, ablative carbon-Phenolic, carbon-carbon heat shields and as hot-structure insulation under these heat shields. Viscose rayon precursor fiber ceased to be made in the US due to EPA restrictions in 1997. While replacements exist, at this time none is equivalent. Cellulose based CF has the lowest thermal conductivity of all available carbon fibers.



SEM of carbon fibers made in the laboratory from IL-processed rayon precursor

A cellulosic fiber process was developed to directly replace viscose, using a new, green process that employs safe and recyclable ILs. Pyrolysis under controlled atmospheres slowly convert this IL processed-cellulosic fiber to carbon fiber. These technologies have all been combined for the first time to make specialized carbon fiber for applications where viscose precursor fibers were once used, particularly for solid rocket motors. (Current TRL:3)

References: [1] Paley, M.S., Karr, L.J., Marone, M.J., and Curreri, P.A. (2009) Space, Propulsion and Energy Sciences International Forum. [2] Marone, M.J., Paley, M.S., Donovan, D.N., and Karr, L.J. (2009) Annual Meeting of the Lunar Exploration Analysis Group, Abstract 2034. [3] Zhang, J, et. al. (2011) Greenhouse Gas Sci Technol. 1:142-159. [4] Gurkan, B.E., et.al. (2010) J. Am. Chem. Soc. 132, 2116-2117.