

REPORT DOCUMENTATION PAGE

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing materials, gathering the data needed, and completing and reviewing this collection of information. Send comments regarding this burden estimate suggestions for reducing this burden to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0714-0128), Washington, DC 20503.

1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE 30 November 2006	3. REPORT TYPE AND DATES COVERED Final: 1 June 2001 to 31 May 2006	
4. TITLE AND SUBTITLE Heavy ion propulsion in the Megadalton range			5. FUNDING NUMBERS AFOSR F49620-01-1-0416	
6. AUTHOR(S) Juan Fernandez de la Mora				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Yale University Mechanical Engineering Depart. PO Box 208286 9 Hillhouse Ave New Haven CT 06520-8286			8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) AFOSR Dr. Mitat A. Birkan AFOSR/NA 875 N.Randolph Street: Ste.325 Arlington VA 22203-1768			10. SPONSORING / MONITORING AGENCY REPORT NUMBER	
11. SUPPLEMENTARY NOTES				
12a. DISTRIBUTION / AVAILABILITY STATEMENT Unlimited			12b. DISTRIBUTION CODE	
DISTRIBUTION STATEMENT A Approved for Public Release Distribution Unlimited				
13. ABSTRACT (Maximum 200 Words) The original project goal was to develop sources of heavy ions for space propulsion, based on Taylor cones of heated ionic liquids (ILs). Many commercially available heated ILs have been discovered that reach the purely ionic regime (PIR) of emissions (no drops), offering a new high-efficiency ion source for electrical propulsion. A few commercial ILs have been found to reach PIR even at room temperature. Later efforts were directed at identifying and testing many non-commercial ILs capable of PIR at room temperature, especially those with high surface tension and high electrical conductivity, which are found to offer the most favorable conditions for electrical propulsion. Basic understanding on Taylor cones of ILs is still incomplete. But they have been seen to have similar advantages to well known liquid metal ion sources (LMIS), in terms of narrow ion energy distribution and micro-Amp current levels. ILs actually outperform liquid metals in many ways, as they run in positive and negative polarity, function at room temperature, offer a much wider range of masses and chemical compositions, are generally less reactive than molten metals, and are expected to form less contaminating plumes.				
14. SUBJECT TERMS			15. NUMBER OF PAGES 13	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT	

FINAL REPORT:

AFOSR F49620-01-1-0416

Heavy ion propulsion in the Megadalton range

1/June/2001 to 31/May/2006

Participants at Yale University:

Principal Investigator: Prof. Juan Fernandez de la Mora

Postdoctoral scholars: Dr. I. Aguirre; Dr. B. K. Ku

Graduate students: Ignacio Romero; Rodrigo Bocanegra; Ismael Guerrero; Carlos Bueno; David Garoz, Maria A. Espina; Sergio Castro, Carlos Larriba

Undergraduates: William Martino, Valeria Fasson

Subcontractors and consultants: Dr. Victor Koch (Covalent); Dr. Leonid Cherney

Collaborators and subcontractors at MIT: Prof. Manuel Martinez Sanchez; Dr. Paulo Lozano; Mr. S. Sümer

Collaborators at Kyoto University: Dr. Y. Yoshida and Prof. G. Saito

Collaboration at USAF Academy: Prof. John Wilkes

Collaboration at Jet Propulsion Laboratory: Dr. Manuel Gamero

Collaboration at Polytechnical Universty Madrid: Prof Francisco Higuera

APPROVED FOR RELEASE
Approved for Public Release
Distribution Unlimited

20061226028

1. Introduction, objectives, and early findings

The original project goal was to develop sources of heavy ions for space propulsion, based on Taylor cones of heated ionic liquids (ILs). Initially we did not know whether or not ILs would be able to operate in the purely ionic regime (PIR) of emissions (no drops), but we expected that they would when heated sufficiently. This point was confirmed experimentally for a group of ILs including several relatively heavy substances [5, 14, 16]. Work with the most interesting among these ILs, EMI-(C₂F₅SO₂)₂N [EMI = 1-ethyl-3-methylimidazolium], has already been published [5], with details on the experimental setup and the means to heat up the liquid. Also published are the temperatures at which PIR sets in for other ILs [10], which are reproduced in Table 1 together with other physical properties of the ILs studied. Details of these measurements are included in a relatively inaccessible Senior Thesis [14], but will be published soon [16]. Some of the relevant time of flight mass spectra (TOF-MS) are included in Figure 1. The charged particle beam produced by the Taylor cone is interrupted at time $t = 0$, and the current I received by a collector located a distance L downstream is then monitored as a function of t . The various steps in the $I(t)$ curves shown in Figure 1 yield the velocity, hence the energy and mass over charge of the various ions and charged drops.

Table I: Ionic Liquids studied in [14], including key physical constants and the temperature T_{PIR} at which their Taylor cones achieve the purely ionic regime. γ = surface tension; ρ = density; K = electrical conductivity

Liquid	γ (dyn/cm)	ρ (g/cm ³)	μ (cP)	K (S/m)	T_{PIR} (°C)
EMI-BF ₄	45.2(23C)	1.24	38	1.4	< 23
EMI-CF ₃ SO ₃	35.8(23C)	1.38	45	0.86	~ 23
EMI-Tf ₂ N	34.9 ^a	1.52	34	0.88	< 82
EMI-(C ₂ F ₅ SO ₂) ₂ N	31.2 ^a	1.6 ^a	61	0.34	< 119
EMI-(CF ₃ SO ₂) ₃ C	32.4 ^a	1.496 ^a	195	0.13	< 216
BMI-(C ₂ F ₅ SO ₂) ₂ N	27.6 ^a	1.425 ^a			< 204
DMPI-(C ₂ F ₅ SO ₂) ₂ N	29.7 ^a	1.506 ^a			< 212
DMPI-(CF ₃ SO ₂) ₃ C	37.8 ^a	1.55 ^a	726	0.046	None
Cyphos-Tf ₂ N	27.4 ^a	1.021 ^a			None
Cyphos-N(CN) ₂	29.2 ^a	0.987 ^a			None
PMI-PF ₃ (C ₂ F ₅) ₃	33.3 ^a	1.59	88.4	0.166	< 157

Cations: EMI = 1-ethyl-3-methylimidazolium; DMPI = 1,2-dimethyl-3-propylimidazolium; BMI = 1-butyl-3-methylimidazolium; PMI = 1-Methyl-3-pentylimidazolium; Cyphos = trihexyltetradecylphosphonium. Anions: Tf₂N = (CF₃SO₂)₂N⁻. ^a Rough measurements without drying precautions.

A key early discovery was that a few exceptional ILs reached PIR even at room temperature (see two top liquids on Table 1). This finding has been published in two full articles from our group [1, 3], which have led to numerous confirmations by others, and to a considerable level of general interest. It has redirected much of our own research and that of other groups working on electrospray propulsion. These more mature developments will be discussed in section 2.

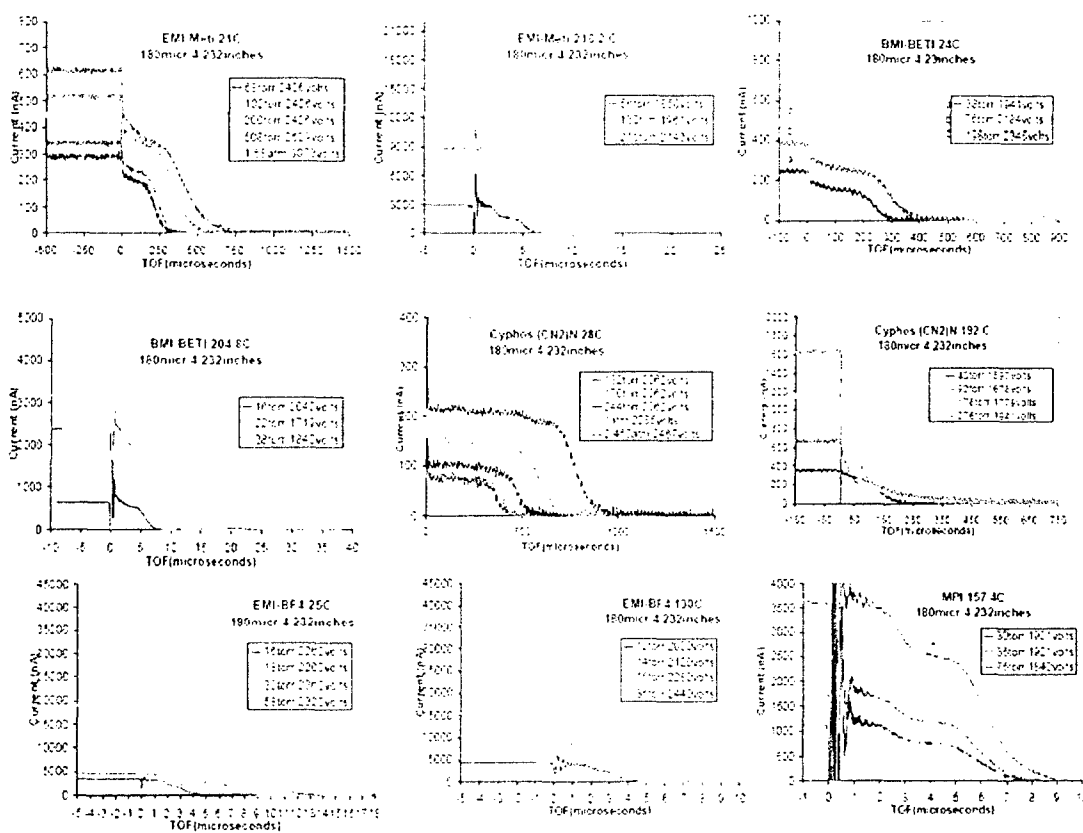


Figure 1: Representative examples of TOF spectra $I(t)$ for several ionic liquids under room and elevated temperature. Some show the transition from the colloidal to the purely ionic regime (EMI-Meti and BMI-Beti), others the absence of the purely ionic regime even at the highest temperatures attained (Cyphos- $N(CN)_2$), and still others the purely ionic regime at room temperature (EMI- BF_4).

1.1 Findings relating to colloidal propulsion

Figure 1 summarizes the main regimes of operation of Taylor cones. To the right one sees the colloidal propulsion region, and to the left the purely ionic region.

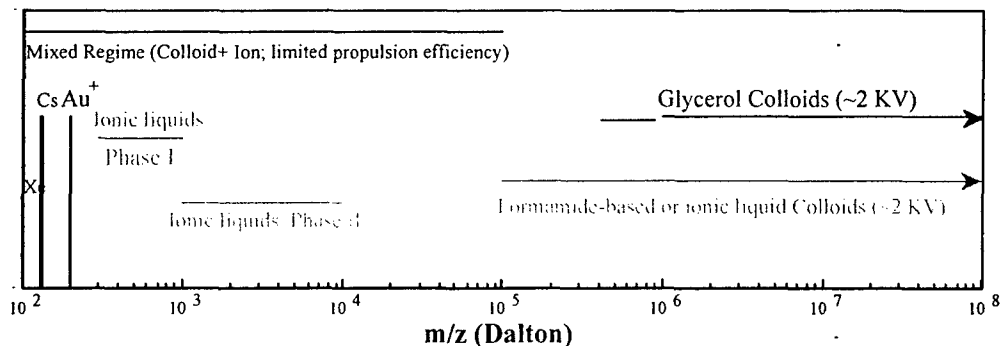


Figure 2: mass over charge ranges offered by existing propellants, including glycerol, formamide and ionic liquids (room temperature molten salts). The gap below 10^5 Dalton may currently be covered only at limited propulsion efficiency in the mixed regime, where both ions and drops are produced.

Colloidal propulsion relies on the production and electrostatic acceleration of charged drops from Taylor cones of electrolytes held in a vacuum. It tends to produce higher thrust levels than PIR, but with modest specific impulses. Our initial work on colloidal propulsion has covered three wide areas.

A: General theory of cone jets. The main contribution was through work of consultant Dr. Leonid Cherney, who made a most valuable contribution to the determination of the point of jet breakup of Taylor cone-jet. This fixes the size of the drops produced. Cherney's work remains unpublished, but its essence has been recently reviewed by the PI [9; section 4.6].

B: Increasing the specific impulse and propulsive efficiency of colloidal propulsion. The highest specific impulse attainable with colloidal propulsion is limited by the onset of ion evaporation, which rapidly reduces propulsion efficiency. Our goal was to delay this limiting phenomenon to smaller and smaller drops. It was achieved by selection of electrolyte ions with high ionization energy. The best candidate found was ammonium nitrate. This study has been published [2].

C: understanding the transition from colloidal to ionic emissions. This item is essential to make progress in understanding PIR. The reason is that a lot is known on the structure of Taylor cone-jets in the absence of ion formation, hence, the rate of ionization from Taylor cones where ion currents are small compared to drop currents is in principle predictable. Our current inability to explain observations under such simple circumstances evidently impairs our ability to understand the far more complex PIR problem. Our limited progress along this line has been submitted for publication [8], but is still unpublished and will be summarized here. The most singular result is the discovery that Taylor cones of certain mixtures of the low-volatility organic solvent propylene carbonate (PC) and the ionic liquid EMI-Tf₂N can operate continuously from the purely colloidal regime (drops only, no ions) to the opposite purely ionic regime (Figure 3).

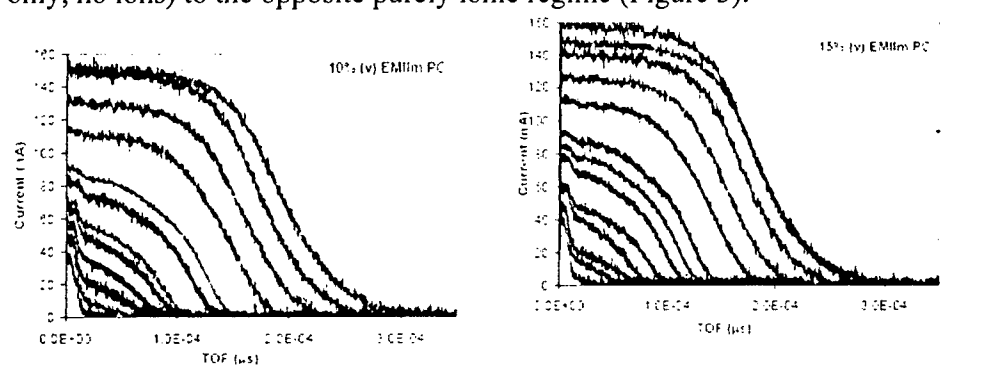


Figure 3: Representative examples of TOF distributions from mixtures of propylene carbonate (PC) and EMI-Tf₂N [denoted EMIIIm in the figure] and PC. Note a clean transition from a purely colloidal to an almost purely ionic behavior.

Numerical calculations in collaboration with Prof F. Higuera permit determining the electric field on the surface of the Taylor cone, which together with conventional ion evaporation theory leads to predictions of the ion current. This current is also measured, but comparison between theory and experiments is disappointing. This is one of the weak links remaining in these studies. We have addressed it first through the studies of Mr. Guerrero [8], then through those of Mrs. Espina, and most recently through those of Mrs.

Fasson. The later study has developed a greatly improved technique to measure very small ion current levels, which will permit comparing theory and experiments under conditions when the cone-jet structure is essentially unaffected by ion evaporation (and is therefore relatively well known). This effort will be continued under a new AFOSR grant.

2. Advances on electrospray propulsion in the purely ionic regime (PIR)

Several types of distinct efforts have been undertaken here:

2.1 Identification of new ILs suitable for PIR operation

This effort has been already described in detail in several conferences and Journal articles now in press or ready to be submitted [10, 11]. A first relatively successful phase was based on commercially available ILs, as summarized in Table I. A second phase was based on a \$12,000 subcontract with the manufacturer of ILs Covalent Associates. This second effort did not produce any promising new IL, but had a positive impact on the grant through the interaction with Covalent's PI Dr. Victor Koch. A third phase involved the synthesis at Yale of a new class of exceptionally conducting ILs. Table II (from [10]) collects the main results from this effort.

Table II. Some characteristics of the ionic liquids synthesized by Garoz [15]

Liquid	MW (amu)	ρ (g cm ⁻³)	γ (dyn cm ⁻¹)	K (S/m)
CH ₃ NH ₃ -COOH	77.09	1.12±0.01		2.9±0.3
(CH ₃) ₂ NH ₂ COOH	91.11	1.06±0.02		6.7±0.9
(CH ₃) ₃ NH-COOH	105.14	1.092±0.002		3.8±0.8
C ₂ H ₅ NH ₃ -COOH	91.11	1.1±0.02	43.8	1.4±0.1
(C ₂ H ₅) ₂ NH ₂ COOH	119.17	1.02±0.02		0.96±0.09
(C ₂ H ₅) ₃ NHCOOH	147.23	1.061±0.005		1.04±0.09
(C ₈ H ₁₇) ₃ NHCOOH	399.71	0.84±0.01		0.014±0.001
(C ₂ H ₅) ₃ NH-CF ₃ O ₃ S	251.3	1.19±0.01		0.46±0.06
(CH ₃) ₂ NH ₂ -Tf ₂ N		1.48±0.01		0.61±0.04
(C ₂ H ₅) ₃ NH-Tf ₂ N		1.41±0.01		0.52±0.06

In spite of the exceptional K values in the Table, none of these liquids achieved PIR operation. However, mixtures of these materials with EMI-BF₄ provided additional important clues. As summarized in Table III, mixtures of Et₃NH-Tf₂N and EMI-BF₄ showed a discontinuous transition between the mixed regime and the PIR.

Table III: Characteristics of mixtures of Et₃NH-Tf₂N + EMIBF₄ as a function of EMI-BF₄ concentration.

Vol %	0	10	30	50	60	65	70	80	100
K(S/m)	0.39	0.53	0.65	0.66	0.74	0.72	0.82	0.99	1.3
Regime	M	M	M	M	M	M&PIR	PIR	PIR	PIR

M = mixed regime; PIR = purely ionic regime; M& PIR means that both regimes are attainable at low and high voltages, respectively.

As discussed in [10] these various early studies suggested that PIR operation would require not only a high electrical conductivity K , but also a relatively high surface tension γ . This realization led to a fourth phase of collaborations with groups that had already synthesized new ILs exhibiting high electrical conductivity. This phase included first some educated guesses of which conducting ILs would also have high surface tension. Since published data on γ were scarce, we developed a technique to accurately measure surface tensions of IL based on the very small samples (Figure 4) we were able to collect from chemist colleagues ($\sim 0.1 \text{ cm}^3$). This measurement method was published [7], and led to the identification of a relatively large number of highly promising ILs. Their list was also reported in [7] prior to their systematic testing as ion sources for space propulsion.

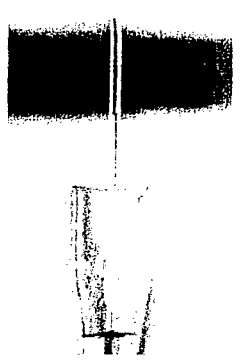


Figure 4: Illustration of the shape of the wetting meniscus at the liquid-glass capillary interfaces (internal, top and external, bottom), and the non-wetting meniscus at the polypropylene reservoir (bottom). The volume of sample is less than 0.1 cm^3

Our new method to measure surface tensions from such tiny samples gave a strong stimulus to our ability to obtain a large number of new substances from collaborating chemists, particularly from Japanese scientists, through a fruitful interaction with Dr. Yoshida. This enabled to test the large number of new substances included in Table IV, in addition to those previously reported in [7]. A considerable number of other IL propellants have subsequently reached our lab, giving rise to a treasure of potentially outstanding propellants. This list is the more remarkable considering that 18 months ago only two ILs capable of PIR were known

Table IV: Surface tensions for the new liquids studied, including in the bottom rows revisions of previously reported values (From reference [10]).

Liquid	γ (at 23°C) (dyn cm ⁻¹)	ρ (g cm ⁻³)	K (S m ⁻¹)	T_m (°C)
EMI-NbF ₆	51.7	1.67	0.85	-1
EMI-TaF ₆	51.3	2.17	0.71	2
EMI-F(HF) _{2.3}	48.0	1.13	10	-65 ^B
EMI-SbF ₆	47.8	1.85	0.62	10
BMI-FeBr ₄	47.1	1.98	0.55	-2
BMI-N(CN) ₂ ^d	46.6	1.06	1.1	-10
C ₆ MI-FeBr ₄	42.0	1.86	0.28	-82(T _g)
C ₆ MI-N(CN) ₂ ^d	40.5	1.04	0.51	-90(T _g)

C ₆ MI-FeCl ₄	39.4	1.33	0.47	-86(T _g)
C ₆ MI-Au(CN) ₂	39.3	1.65	0.081 ^c	13
C ₈ MI-FeBr ₄	38.1	1.74	0.14	-81(T _g)
C ₈ MI-FeCl ₄	37.2	1.28	0.22	-84(T _g)
C ₈ MI-Au(CN) ₂	36.0	1.59	0.056 ^c	-61(T _g)
EMI-GaCl ₄	48.6(50) ^{a, b}	1.53	2.2	11
EMI-FeCl ₄	47.3(47.7) ^{a, b}	1.42	2.0	18
BMI-GaCl ₄	43.6(41.5) ^a	1.43 ^c	0.95 ^c	-88(T _g)
EMI-(C ₂ F ₅ SO ₂) ₂ N	28.7 ^b	1.6 ^c	0.34	-1(^j)
PMI-(C ₂ F ₅) ₃ PF ₃	30.3	1.59 ^h	0.166	<-50
EMI-TfO	38.3(39.2) ^a	1.39	0.86	-9
EMI-BF ₄	45.2(44.3) ^a	1.24 ⁱ	1.36	11
EMI-Tf ₂ N	35.8(35.2) ^a	1.52	0.88	-1
DMI-N(CN) ₂ ^d	54.9(61.6) ^a	1.14	3.6	34

^a γ values in brackets are less reliable than the new values. ^b 21°C; ^c Rough measurements without drying precautions. ^d See Y. Yoshida, O. Baba, G. Saito, to be submitted to J. Phys. Chem. B. ^e Y. Yoshida, unpublished data. ^f Fuller, J.; Carlin, R. T.; Osteryung, R. A.. J. Electrochem. Soc. 1997, 144, 3881-3886. ^g R. Hagiwara, K. Matsumoto, Y. Nakamori, T. Tsuda, Y. Ito, H. Matsumoto, K. Momota, J. Electrochem. Soc. 2003, 150 (12), D195–D199. ^h Merck home page

2.2 Testing of new ILs as electrospray ion sources for electrical propulsion

The systematic testing as ion sources of a selected group of the many new propellants identified has been reported in [11], which was also presented at AIAA's 2006 joint propulsion conference, and published in the proceedings. [11] is just a more polished version of that conference paper. The main conclusions of these studies are summarized in section 2.3 below.

2.3 Basic understanding of fluid properties required for PIR operation

The main conclusion derived from our many tests of ionic liquids as ion sources for electrical propulsion is that already anticipated, namely, that a combination of high electrical conductivity and high surface tension is desirable for optimal operation. Perhaps the best fuel identified to date is EMI-GaCl₄, but several others are comparable.

2.4 Studies on the role of the ion source on propulsive performance

Our discovery of the purely ionic regime of ILs has sparked a number of related studies in other research groups (MIT, Hanscom Air Force Laboratory) and industry (CAC, Busek). Of particular note has been the discovery by Lozano and Martinez Sanchez at MIT of a new type of ion source based on an externally wetted sharpened and electrochemically roughened tungsten needles. This source is referred to as ILIS (ionic liquid in source). According to our MIT colleagues, this source is able to produce PIR beams of ILs of modest surface tension or electrical conductivity. Although these sources tend to yield modest ion currents, the quality of the beam is outstanding, which implies relatively high propulsion efficiency. In view of the potential practical importance of these sources, we have collaborated with the MIT group in testing them with a wider

range of ILs, and comparing them with conventional sources based on internally fed capillary tubes. This collaboration was undertaken with a subcontract to MIT, where MIT provided us with an ILIS ion source fitted to our apparatus. Our first results were presented at the joint propulsion conference in 2006, with details included in the proceedings as an AIAA paper. This reference is about to be sent for journal publication including minor polishing details [12], with main conclusions summarized in Figure 5. The physical properties of the ILs involved are collected in Table V. We confirm entirely the conclusions from the MIT group, and note in addition that PIR operation at 23 °C is viable even in far less conducting and relatively viscous liquids than previously imagined under the most optimistic conditions.

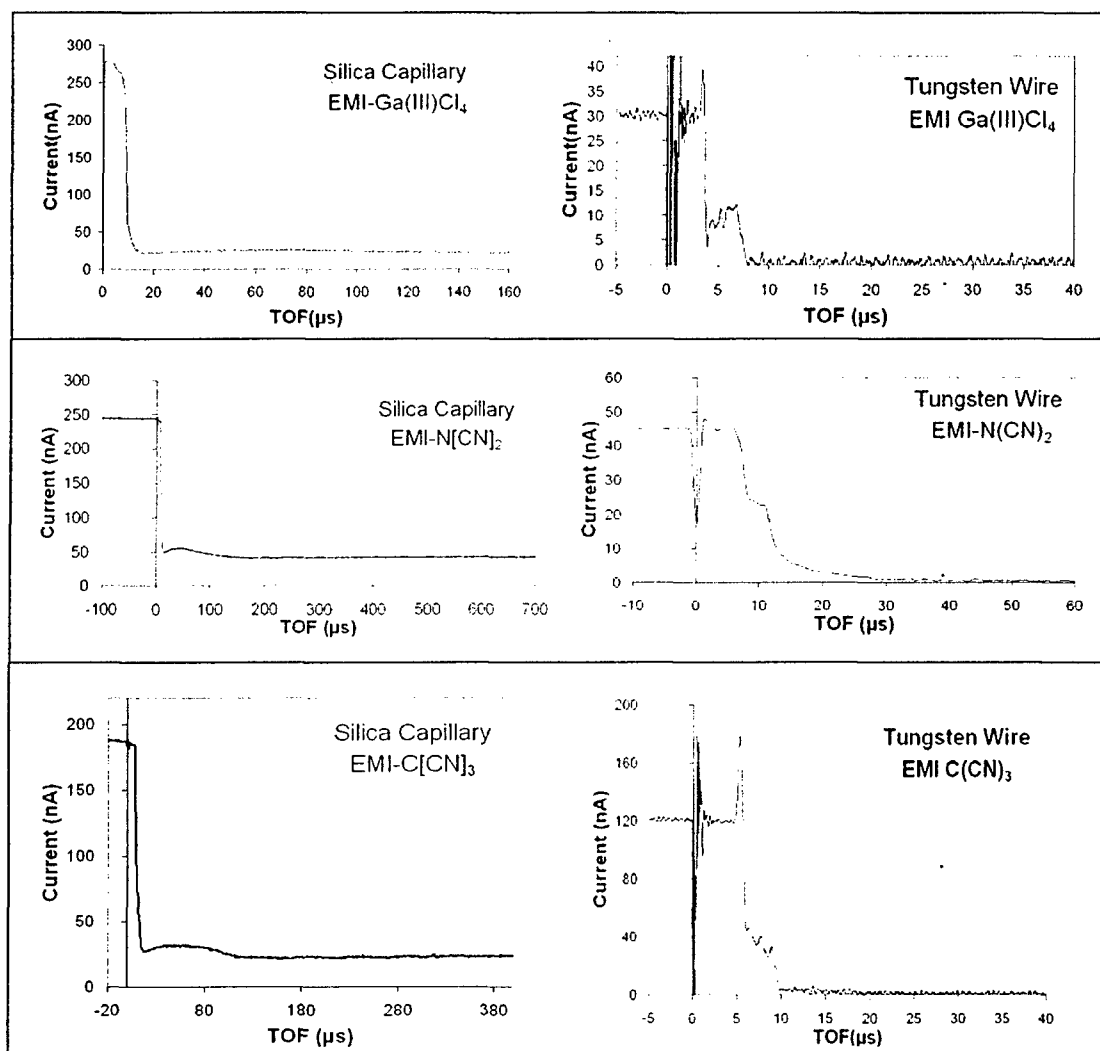


Figure 5. Comparison of the TOF spectra obtained for the ILs with high surface tension and high electrical conductivity with the capillary source (left) and the ILIS (right).

2.5 High quality ion sources in the KiloDalton range.

An extension of the previous striking results on the advantages of ILIS sources has recently been submitted for publication [13]. In it, we extend prior work to two even less conducting ILs, whose special interest is associated to the relatively high mass of their cations and anions.

Table V: Physical properties of the ILs tested.

Liquid	γ (23°C) (dyn cm ⁻¹)	ρ (20°C) (g cm ⁻³)	K (25°C) (S m ⁻¹)	T_m (°C)
EMI-GaCl ₄	48.6(50) ^{a, b}	1.53	2.2	11
EMI-N(CN) ₂	42.6 ^c	1.08	2.8	-12
EMI-C(CN) ₃	47.9 ^c	1.11	2.2	-11

^b 21°C; ^c 25°C. T_g is the glass transition temperature, which for the last two liquids listed is the temperature at which transformation from liquid to solid occurs.

Figure 6 summarizes our results, showing rather sharp steps of various ions emitted in positive and negative mode for the ILs C₅MI-(C₂F₅)₃PF₃ and (EMI-(C₂F₅SO₂)₂N) [C₅MI = 1-methyl-3-pentylimidazolium]. The emissions are purely ionic, though they include unusually large ion clusters

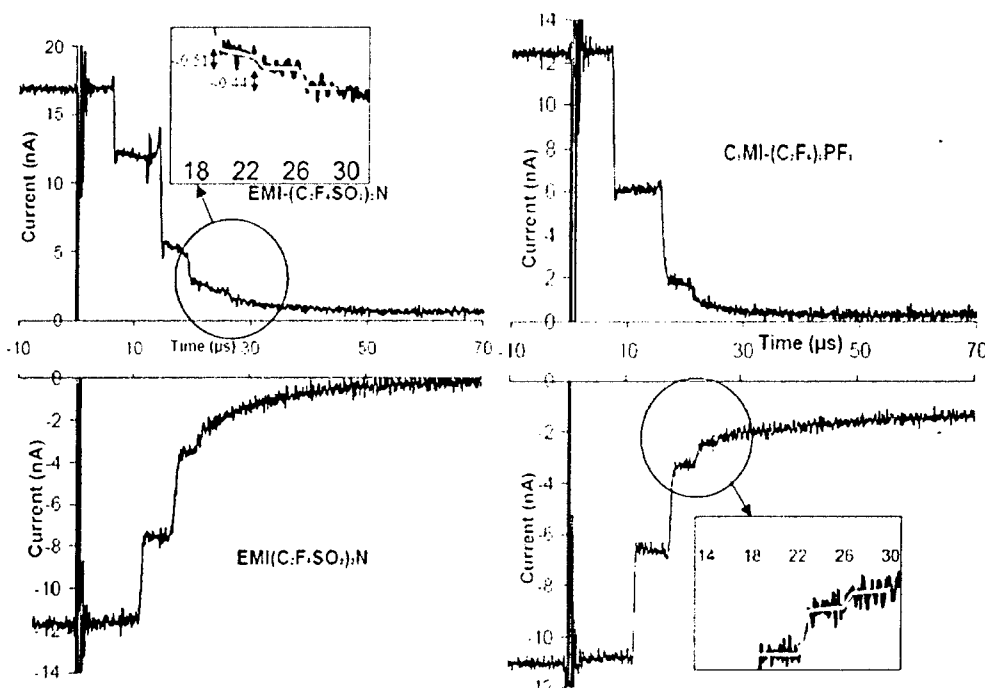


Figure 6: TOF-MS of the emissions from Taylor cones of the ionic liquids: C₅MI-(C₂F₅)₃PF₃ (right), and EMI-(C₂F₅SO₂)₂N (left). Top, positive electro spray; bottom, negative electro spray. The figure shows ion currents of about 0.5 nA at masses close to 2000 amu, both in positive and negative mode.

3. Conclusions

A five-year effort on the previously virgin subject of Taylor cones of molten salts for electrical propulsion has opened up a rather rich field, with dozens of potential IL propellants offering splendid performance in a wide range of masses, in some cases

reaching well above 1000 amu. Although the basic understanding of this phenomenon is still fairly incomplete, it is already clear that the new sources have advantages comparable to the much better known liquid metal ion sources (LMIS), in terms of beam quality, narrow energy distribution and current levels in the range of microamperes. The new sources, however, outperform LMIS in many ways, as they run in positive and negative polarity, function at room temperature, and offer a much wider range of masses and chemical composition. Also, ILs are generally less reactive than molten metals, and are expected to form less contaminating plumes.

Journal articles, submitted and appeared

1. I. Romero-Sanz, R. Bocanegra, J. Fernández de la Mora and M. Gamero-Castaño. Source of heavy molecular ions based on Taylor cones of ionic liquids operating in the pure ion evaporation regime, *Journal of Applied Physics*. Vol.94, No 5, 3599-3605, September 2003.
2. Rodrigo Bocanegra, Juan Fernandez de la Mora and Manuel Gamero, Ammonium electrolytes quench ion evaporation in colloidal propulsion, *Journal of Propulsion and Power* 20 (4): 728-735, 2005
3. I. Romero-Sanz and J. Fernandez de la Mora, Spatial structure and energy distribution of electrosprays of ionic liquids in vacuo, *J. Applied Physics*, 95 (4): 2123-2129, 2004
4. Bon Ki Ku and Juan Fernandez de la Mora, Cluster ion formation in electrosprays of acetonitrile seeded with ionic liquids, *J. Phys. Chem. B*, **108**, 14915-14923, 2004
5. I. Romero-Sanz, I. Aguirre-de-Carcera and J. Fernandez de la Mora, Ionic propulsion based on heated Taylor cones of ionic liquids, *J. Prop. & Power*, 21, No. 2, 239-242, 2005
6. Bon Ki Ku and Juan Fernandez de la Mora, Evaporation Kinetics of Tetra-alkylammonium Ions from Charged Formamide Drops, *J. Physical Chemistry*, **109**(22), 11173-11179, 2005.
7. W. Martino, J. Fernandez de la Mora, Y. Yoshida, G. Saito and J. Wilkes, Surface tension measurements of highly conducting ionic liquids, *Green Chemistry*, 2006, **8**, 390-397
8. I. Guerrero, R. Bocanegra, J. Fernandez de la Mora and F.J. Higuera, Ion evaporation from Taylor cones of propylene carbonate mixed with ionic liquids, Submitted to *J. Fluid Mechanics*, February 2005
9. J. Fernandez de la Mora, Fluid dynamics of electrosprays, *Annual Review of Fluid Dynamics*, **39**, 217-243 (2007).
10. C. Larriba, D. Garoz, C. Bueno, I. Romero-Sanz, S. Castro, J. Fernandez de la Mora, Y. Yoshida, G. Saito, R. Hagiwara, K. Matsumoto, J. Wilkes, Taylor cones of ionic liquids as ion sources: The role of electrical conductivity and surface tension, in *Ionic Liquids: Not Just Solvents Anymore*. J. Brennecke, R. D. Rogers and K. R. Seddon, editors, ACS, 2006
11. D. Garoz, C. Bueno, C. Larriba, S. Castro, and J. Fernandez de la Mora, Taylor cones of ionic liquids from capillary tubes as sources of pure ions for electrical propulsion, submitted to *J. Propulsion and Power*, December 2006
12. S. Castro, C. Larriba, and J. Fernandez de la Mora, P. Lozano and S. Suner, Capillary vs. externally wetted ionic liquid ion sources, submitted to *J. Propulsion and Power*, December 2006
13. C. Larriba, S. Castro, and J. Fernandez de la Mora, P. Lozano, Monoenergetic source of KiloDalton ions from Taylor cones of ionic liquids, Submitted to *J. Applied Phys.* Nov/2006

Other non-archival references

14. Romero-Sanz I., "Propulsión iónica y coloidal por atomización electrostática de sales fundidas. Aplicación a microsátélites". Masters Thesis. 2002. Universidad Carlos III de Madrid. Spain. An expanded version is included in Romero's PhD Thesis, *Propulsión y iónica y coloidal por atomización electrostática*, Universidad Carlos III, Madrid, Spain (2006)
15. D. Garoz, "Síntesis, estudio y mezclas de nuevos combustibles basados en líquidos iónicos para la propulsión eléctrica a partir de conos de Taylor en vacío" (Synthesis, study and mixtures of new ionic liquid-based propellants for electrical propulsion from Taylor cones in vacuum), Proyecto fin de carrera (Senior Thesis), Universidad Politécnica de Madrid, Marzo 2004

Articles in preparation

- 16 I. Romero-Sanz and J. Fernandez de la Mora, The purely ionic regime in heated Taylor cones of ionic liquids, in preparation for *Phys Fluids*, 2006

4 Relevance/transitions

There is to date no commercial effort in the US directed at the kind of ion propulsion explored here for the first time, although its apparent superiority over the European competitor scheme FEEP (based on LMIS) has led to a level of interest on the part of the companies Busek Co. Inc. and Connecticut analytical Corporation (CAC). The AFOSR is currently supporting several Phase II SBIRs in this field, two of which are based on the IL technology developed under this grant. Busek is also using IL based colloidal sources for their NASA DR7 mission, based on some of the fuels we have first proposed and characterized as part of this research.

Inventions

The following invention was reported formally to Yale University, and led to a provisional patent application. Subsequently, Yale decided not to pursue the option of applying for a non-provisional patent, so this invention has now become public domain. The invention is not directly relevant to electrical propulsion because the salt Dimethyl ammonium formate is excessively volatile.

David Garoz and Juan Fernandez de la Mora, Dimethyl ammonium formate: an ionic liquid with an exceptional electrical conductivity; Provisional patent application submitted to USPTO, 2003

Interactions: The PI has been an invited speaker in two special sessions on ionic liquids at annual meetings of the American Chemical Society, one held in New York, the other in Atlanta (2006). This has provided excellent opportunities to interact with chemist experts in IL synthesis.

Collaborations: The visibility of our work under this program has been most beneficial for its progress, as it has elicited the interest and intellectual support from a number of expert colleagues in the field of ionic liquids. Most important has been the involvement of Professor John Wilkes (Air Force Academy, Colorado Springs), one of the leading world experts in the field. We have received also strong backing from the company

Covalent, a leading industrial developer of ionic liquids in the US. This support has involved advise on new syntheses, and gifts of some of the most interesting commercial samples we have tested. Another leading supplier of ionic liquids, the Canadian company Cytec, has also provided us with many samples of their Cyphos products. Colleagues at Kyoto University have provided the largest number of ILs used. Dr. Yoshida has been the leading contributor to this most fruitful collaboration. Aside from those cited, we have collaborated closely and freely exchanged information with the MIT group of Martinez Sanchez, Busek, Connecticut Analytical Corporation (Bethany, Connecticut), and the group of Dr. Dressler at Hanscom Air Force Base

Transitions: The use of Taylor cones of ionic liquids run in the purely ionic regime has attracted considerable interest in the short time following our first related report. Busek and CAC have current Phase II STTR projects with the AFOSR to exploit this new phenomenon for developing two-dimensional thrusters. Professor M. Martinez-Sanchez of MIT and Dr. R. Dressler (Hanscom) have been using our ionic liquids already for several years. Our introduction of ionic liquids has also had a fair influence on work carried for NASA. For instance, Busek's large effort to develop the thrusters for NASA's disturbance reduction program is being based not on formamide as originally planned, but on the ionic liquid EMI-Tf₂O which we first introduced in the propulsion context. Work carried by Connecticut Analytical for NASA-JPL was also based exclusively on ionic liquids.
