



Compact, Highly Stable Ion Atomic Clock

This high-precision clock is designed for navigation and radio science applications.

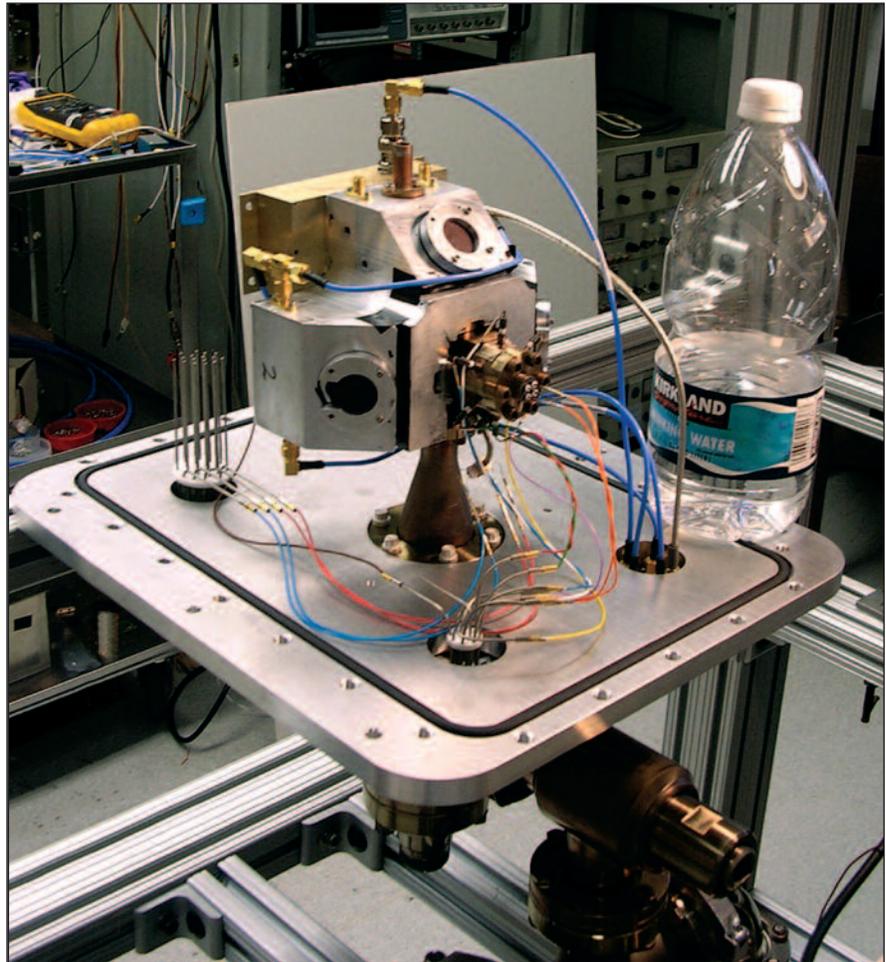
NASA's Jet Propulsion Laboratory, Pasadena, California

A mercury-ion clock now at the breadboard stage of development (see figure) has a stability comparable to that of a hydrogen-maser clock: In tests, the clock exhibited an Allan deviation of between 2×10^{-13} and 3×10^{-13} at a measurement time of 1 second, averaging to about 10^{-15} at 1 day. However, the clock occupies a volume of only about 2 liters — about a hundredth of the volume of a hydrogen-maser clock. The ion-handling parts of the apparatus are housed in a sealed vacuum tube, wherein only a getter pump is used to maintain the vacuum. Hence, this apparatus is a prototype of a generation of small, potentially portable high-precision clocks for diverse ground- and space-based navigation and radio science applications. Furthermore, this new ion-clock technology is about 100 times more stable and precise than the rubidium atomic clocks currently in use in the NAVSTAR GPS Earth-orbiting satellites.

In this clock, mercury ions are shuttled between a quadrupole and a 16-pole linear radio-frequency trap. In the quadrupole trap, the ions are tightly confined and optical state selection from a ^{202}Hg radio-frequency-discharge ultraviolet lamp is carried out. In the 16-pole trap, the ions are more loosely confined and atomic transitions resonant at frequency of about 40.507 GHz are interrogated by use of a microwave beam at that frequency.

The trapping of ions effectively eliminates the frequency pulling caused by wall collisions inherent to gas-cell clocks. The shuttling of the ions between the two traps enables separation of the state-selection process from the clock microwave-resonance process, so that each of these processes can be optimized independently of the other.

The basic ion-shuttling, two-trap scheme as described thus far is not new: it has been the basis of designs of prior larger clocks. The novelty of the present development lies in major redesigns of its physics package (the ion traps and the vacuum and optical sub-



The **Physics Package** of the breadboard liter-sized ion clock is shown here with a connection to an ultrahigh-vacuum pump. The base plate, not part of the package, is used for thermo-vacuum tests of the package. The liter water bottle is shown for scale.

systems) to effect the desired reduction of size to a volume of no more than a couple of liters. The redesign effort has included selection of materials for the vacuum tube, ion trap, and ultraviolet windows that withstand bakeout at a temperature of $\approx 450^\circ\text{C}$ in preparation for sealing the tube to contain the vacuum. This part of the redesign effort follows the approach taken in the development of such other vacuum-tube electronic components as flight traveling-wave-tube amplifiers having operational and shelf lives as long as 15 years.

The redesign effort has also included a thorough study of residual-gas-induced shifts of the ion-clock frequency and a study of alternative gases as candidates for use as a buffer gas within the sealed tube. It has been found that neon is more suitable than is helium, which has been traditionally used for this purpose, in that the pressure-induced frequency pulling by neon is between a third and a half of that of helium. In addition, because neon diffuses through solids much more slowly than does helium, the loss of neon by diffusion over the operational lifetime is expected to be negligible.

The redesign of the optical system has included the formulation of a modular optical-system design that integrates lenses, mirrors, the lamp and its radio-frequency exciter, a photomultiplier tube, and pulse-generation electronic circuitry, into a small package that is attached to the vacuum tube in alignment with the optical ports on the surface of the tube and with the ion trap inside the tube. A reference mag-

netic-field coil, an inner magnetic shield, and a 40.507-GHz microwave feed with window have also been incorporated.

This work was done by John Prestage of Caltech for NASA's Jet Propulsion Laboratory.

In accordance with Public Law 96-517, the contractor has elected to retain title to this invention. Inquiries concerning rights for its commercial use should be addressed to:

Innovative Technology Assets Management
JPL
Mail Stop 202-233
4800 Oak Grove Drive
Pasadena, CA 91109-8099
(818) 354-2240
E-mail: iaoffice@jpl.nasa.gov
Refer to NPO-43075, volume and number of this NASA Tech Briefs issue, and the page number.

LiGa(OTf)₄ as an Electrolyte Salt for Li-Ion Cells

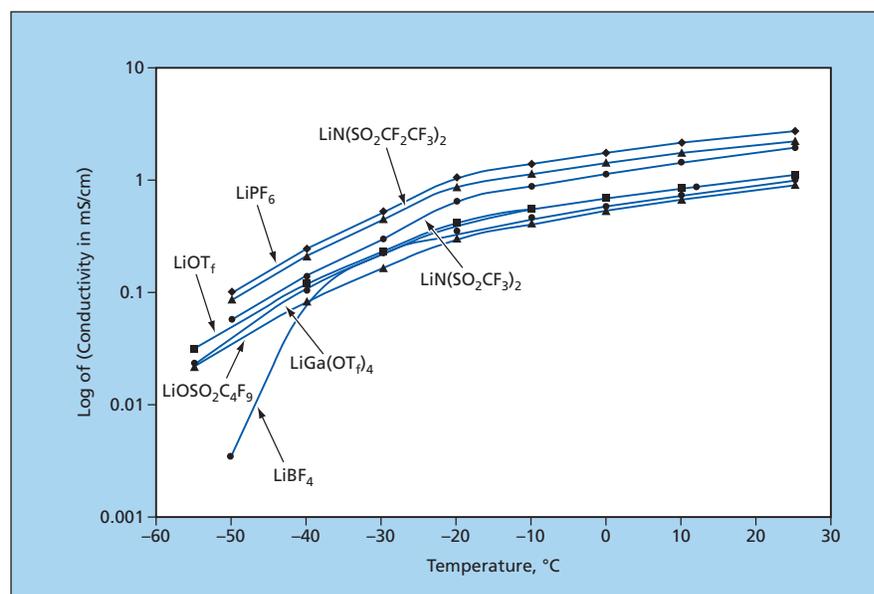
This salt could improve rechargeable lithium-ion cell performance.

NASA's Jet Propulsion Laboratory, Pasadena, California

Lithium tetrakis(trifluoromethanesulfonato)gallate [abbreviated "LiGa(OTf)₄" (wherein "OTf" signifies trifluoromethanesulfonate)] has been found to be promising as an electrolyte salt for incorporation into both liquid and polymer electrolytes in both rechargeable and non-rechargeable lithium-ion electrochemical cells. This and other ingredients have been investigated in continuing research oriented toward improving the performances of rechargeable lithium-ion electrochemical cells, especially at low temperatures.

This research at earlier stages, and the underlying physical and chemical principles, were reported in numerous previous *NASA Tech Briefs* articles. As described in more detail in those articles, lithium-ion cells most commonly contain non-aqueous electrolyte solutions consisting of lithium hexafluorophosphate (LiPF₆) dissolved in mixtures of cyclic and linear alkyl carbonates, including ethylene carbonate (EC), propylene carbonate (PC), dimethyl carbonate (DMC), diethyl carbonate (DEC), and ethyl methyl carbonate (EMC). Although such LiPF₆-based electrolyte solutions are generally highly ionically conductive and electrochemically stable, as needed for good cell performance, there is interest in identifying alternate lithium electrolyte salts that, relative to LiPF₆, are more resilient at high temperature and are less expensive.

Experiments have been performed on LiGa(OTf)₄ as well as on several other candidate lithium salts in pursuit of this interest. As part of these experiments, LiGa(OTf)₄ was synthesized by the reaction of Ga(OTf)₃ with an equimolar portion of LiOTf in a solvent consisting of anhydrous acetonitrile. Evaporation of the solvent yielded



Ionic Conductivities of 0.10 M Solutions of the indicated lithium salts in equal volume parts of PC and DMC were measured at temperatures from -50 to +25 °C. The salts other than LiPF₆, including LiGa(OTf)₄ have been investigated as candidates to supplant LiPF₆.

LiGa(OTf)₄ as a colorless crystalline solid. The LiGa(OTf)₄ and the other salts were incorporated into solutions with PC and DMC. The resulting electrolyte solutions exhibited reasonably high ionic conductivities over a relatively wide temperature range down to -40 °C (see figure). In cyclic voltammetry measurements, LiGa(OTf)₄ and the other salts exhibited acceptably high electrochemical stability over the relatively wide potential window of 0 to 5 V versus Li⁺/Li. ¹³C nuclear-magnetic-resonance measurements yielded results that suggested that in comparison with the other candidate salts, LiGa(OTf)₄ exhibits less ion pairing.

Planned further development will include optimization of the salt and sol-

vent contents of such electrolyte solutions and incorporation of LiGa(OTf)₄ into gel and solid-state polymer electrolytes. Of the salts, LiGa(OTf)₄ is expected to be especially desirable for incorporation into lithium polymer electrolytes, wherein decreased ion pairing is advantageous and the large delocalized anions can exert a plasticizing effect.

This work was done by V. Prakash Reddy of the University of Missouri-Rolla; G.K. Syria Prakash, Jinbo Hu, and Ping Yan of the University of Southern California; and Marshall Smart, Ratnakumar Bugga, Keith Chin, and Subbarao Surampudi of Caltech for NASA's Jet Propulsion Laboratory. For more information, contact iaoffice@jpl.nasa.gov. NPO-41516