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C_2^- Ion as Impurity from Halogen Ion Source and a Possibility of Its Application to Reaction Kinetics Studies

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Synopsis. Negative ions from a hot LaB_6 surface were studied with a quadrupole mass filter. C_2^- ion was formed *via* a charge exchange process. About 10^{-11} A of mass-selected C_2^- ion current was obtained above 40 eV of ion energies. A possibility of employing this to study a reaction kinetics is discussed.

We constructed an ion source for the negative atomic halogen ions based on surface ionization[1,2] and successfully applied it to a study on the ion-molecule reactions of $Br^- + CH_4$,[3] $Br^- + CH_3F$.[4] The ion source delivered *ca.* 10^{-8} A of the atomic halogen ion current above 20 eV of the ion energy with caesium halide as the source material and LaB_6 as ionizing material. The ion beam was checked in terms of energy spread and purity. The intrinsic energy spread at the zero energy was found to be 0.55 eV[2] from measurement of dependence of the energy spread on ion energy with an electrostatic energy analyzer of parallel plate type. The purity of the beam was studied by mass analysis with a RF quadrupole mass filter. The result indicated that the ion beam is quite pure, no measurable amounts of impurity ions being observed.

In the present paper we report on the ionic impurities in the ion beam observed with more sensitive electrometer under optimal conditions for the minority ions but not necessarily for the main ion, and discuss their possible use as an ion beam. In the case of caesium bromide as the source material such negative ions as F^- ($m/e=19$), C_2^- ($m/e=24$), CN^- ($m/e=26$), O_2^- ($m/e=32$), and Cl^- ($m/e=35$ and 37) were observed as the minority ions besides Br^- ion, although their ion intensities were less than 100 ppm of Br^- ion under normal operating conditions and *ca.* 10^{-11} A for C_2^- ion with a kinetic energy of 40 eV and less for others under optimal conditions. As the Br^- ion,[1,2] the halogen ions Cl^- and F^- are formed by a negative surface ionization on the hot LaB_6 surface which has a small work function of 2.6 eV,[5] due to the large electron affinities of their neutral species, Br, Cl, and F being 3.54 eV, 3.76 eV and 3.58 eV, respectively.[6] Since the neutral species of these minority halogens exist as an impurity in CsBr, the contribution of the corresponding ions can be in the same order of magnitude as an impurity content.

Of the minority ions, the particularly interesting one is C_2^- ion which is the second abundant ionic species next to Br^- ion in the mass spectrum. Contrary to the halogens, the neutral species for C_2^- and CN^- ions may not be impurities of the source material but are formed only at the hot graphite surface as seen in an emission study with a graphite electrode. Furthermore, C_2 has the electron affinity of 3.54 eV[6] which is large enough to be surface ionized on the hot LaB_6 surface. However, the experimental result shows that no such ion was formed when no CsBr was supplied. Thus, it is concluded that C_2^- ion is not produced by the surface ionization. As an alternative process for the formation of this ion we assign the accidental near resonance charge exchange between Br^- and C_2, since the electron affinity of C_2 matches that of Br. The cross section for this process is supposed to be large, possibly in the order of 10×10^{-16} cm^2.[7] However, the correct mechanism for C_2^- ion formation remains open to question.

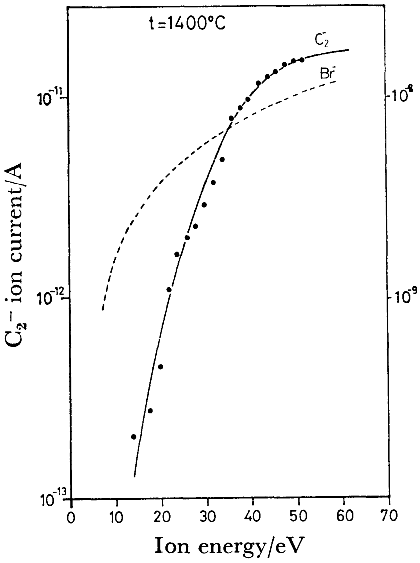

Fig. 1. Energy dependence of C_2^- ion current with CsBr at 1400 °C.

Although the ion source was originally designed and operated only for the sake of the major ion, we tested the possibility of employing it as the beam source for the minority ions. The C_2^- ion current was measured under the optimum operating conditions in order to get a maximum current. The variation of the ion intensity as a function of the ion energy is shown in Fig. 1. The ion intensity of C_2^- ion is *ca.* 10^{-11} A above 40 eV, declining sharply for lower ion energies. The behavior is similar to that of the major ion indicating a space charge effect. However, the intensities for these ions can not be directly compared since they were measured

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under optimal conditions for each ion.

The energy spread of the C_2^- ion beam was also measured, an intrinsic energy spread of *ca.* 0.55 eV being obtained as the major ion by extrapolating an energy spread-ion energy curve to zero energy.

In applying this ion source to the reaction kinetics for the minority ions, however, a mass discrimination of the desired ion from others, especially the major ion, is necessary prior to the deceleration and focussing of ion beam onto a scattering cell. This can be easily achieved with a small permanent magnet or a RF quadrupole mass filter, since only a moderate mass resolution is required. Furthermore, a very small number of ionic products can be detected by mass analysis in combination with a pulse counting technique.

Since C_2^- ion is very stable and an important precursor in flame reactions reacting with such molecules as H_2, H_2O and hydrocarbons, it would be interesting to study such ion-molecule reactions by means of the present source.

Experimental

The apparatus consists of an ion emitter, a magnet, an acceleration-deceleration multistage lens and a RF quadrupole mass filter. The ion source chamber and the chamber which accomodates a mass filter are separately pumped with oil diffusion pumps. The operating pressures of both chambers are maintained below 10^{-6} Torr (1 Torr=133.322 Pa). The ion source, unless otherwise specified, is constructed of stainless steel. The main part of the ion source is the ion emitter made of a rear-fed layer of LaB_6 as the ionizing material (Fig. 2).

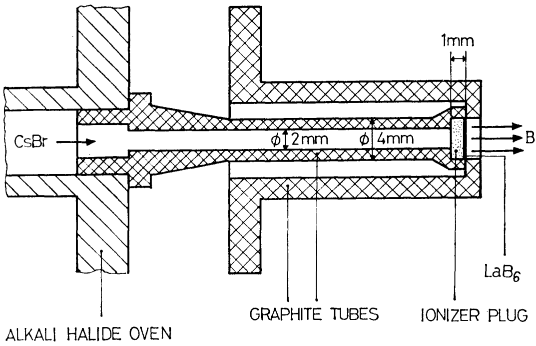

Fig. 2. Cross sectional view of the alkali halide type ion emitter.

Graphite (type EK 87, Ringsdorff, Bonn) was used as a structural material. However, since graphite does not bind firmly with LaB_6, LaB_6 powder was suspended in a small amount of methanol and then pressed onto the porous graphite plug; after evaporation of the solvent in a vacuum, it was heated to its operating temperature, affording a mechanically stable sedimentary layer of LaB_6. The concentric graphite tubes are in contact with each other at their front ends and heated by an alternating current of *ca.* 100 A to 1300 °C in the region of the ionizing area. The desired halogen is supplied as caesium halide from the oven heated by means of a molybdenum wire to 500 °C or higher. The vapor passes the inner graphite tube and diffuses through the porous graphite plug and the sedimentary layer of LaB_6, at which the alkali halide molecules are eventually surface ionized. The negative ions thus formed are extracted and simultaneously accelerated in order to avoid a space charge effect. After being focused by a couple of lenses and then decelerated to the desired ion energy equal to the voltage applied to the ion emitter, the ions are subjected to mass analysis with a RF quadrupole mass filter (Extranuclear Laboratries, Model 324-9) and collected on a cylindrical Faraday cup, the current from which is measured with a Keithley 414S Picoammeter. At the operating temperature 1300 °C, the LaB_6 surface also emits electrons, in a number at least three orders of magnitude greater than that of major negative ions. The electrons are removed from the ions by means of a magnetic field perpendicular to the beam axis. The ions proceed practically unaffected by the field due to their far larger masses. When necessary, energy analysis is carried out after deceleration by means of an electrostatic energy analyser.

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