DEVELOPMENT OF AN INERT GAS CONDENSATION BASED ION SOURCE FOR THE GENERATION OF STRONG BEAMS OF LARGE CLUSTER IONS

H. W. SARKAS, L. H. KIDDER, J. G. EATON, K. M. MCHUGH, AND K. H. BOWEN
Department of Chemistry, Johns Hopkins University, Baltimore, MD 21218

ABSTRACT

We report on the further development of an ion source for producing intense, continuous beams of large positive and negative cluster ions comprised of high temperature materials. This device, the Smoke-Ion Source, is the result of combining inert gas condensation methods with techniques for injecting electrons directly into expanding jets. We demonstrate the capability of this ion source to generate strong beams of cluster ions comprised of materials including metals, semiconductors, and metal oxide ceramics.

INTRODUCTION

In both science and high technology there is a need for high intensity sources of large cluster ions comprised of high temperature materials. In recent years, interest has continued to grow in the potential applications of clusters and cluster ions in the formation of new materials, thin film formation, size-specific catalyst preparation, ion beam sputtering, and ion lithography [1-3]. Here, we report on the continuing development and characterization of a source for generating intense, continuous beams of large cluster ions from high temperature materials [4,5]. This device is the result of combining the inert gas condensation method with techniques for injecting electrons directly into expanding jets. Inert gas condensation is a proven approach for generating strong beams of large neutral clusters comprised of high temperature materials [6-13]. In inert gas condensation cells, an oven evaporates the material of interest into a bath of cool inert gas. The evaporated material supersaturates in this cool environment and nucleates to form a dilute smoke composed of ultrafine particles and clusters. The inert gas, along with its entrained smoke, exits the cell through a small aperture into a high vacuum region where it forms a beam.

Several investigators have generated positive cluster ions from inert gas condensation neutral cells, usually in the course of mass spectrometric characterization studies. In each case, ionization was carried out well downstream of the cells' exit apertures by subjecting the neutral cluster beams to either electron bombardment or to photoionization [8-13]. In the present work however, electrons from a biased filament are injected in a close-coupled manner directly into the weak jet expansion of the smoke-containing inert gas as it leaves the condensation cell. The injection of low energy electrons directly into the high density region of supersonic expansions has been shown to be a highly efficient method for generating beams of both positive and negative cluster ions [14-16]. This arrangement allows the generation of <u>intense</u> beams of large positive and negative cluster ions. We refer to the unique union of these two techniques as the Smoke-Ion Source. Below, we describe the Smoke-Ion Source along with its associated apparatus,

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and present the results of mass spectrometric investigations involving cluster ions of lead, lead sulfide, lithium, sodium, and magnesium; mixed cluster ions of lithium and magnesium; cluster ions of lithium oxide, magnesium oxide, and lithium-magnesium oxide; and very preliminary results on carbon cluster anions and on cluster anions generated from sodium chloride.

EXPERIMENTAL

The Smoke-Ion Source has been described previously [1,2], and only a brief description is given here. A material of interest is evaporated in a radiation shielded crucible region (capable of achieving temperatures to 3000 K) by resistive heating. The crucible region is separated from the inert gas condensation cell by a water-cooled copper box which thermally isolates the cool inert gas from the high temperature environment of the crucible region. Vapor effusing from the crucible enters the condensation cell, which typically contains from 0.5 to 10 torr of helium and can be maintained at constant temperatures between 77 K and 285 K by a coolant reservoir. The cool inert gas thermally quenches the vapor, causing supersaturation with subsequent nucleation and cluster growth. The condensation cell is coupled to high vacuum by a small (1.0-2.5 mm diameter) aperture, creating a flow of helium which entrains the clusters and transports them into the high vacuum region via a weak jet expansion. A negatively biased hot filament injects low energy electrons into the smoke-containing helium flow immediately as it exits the aperture. The presence of axial magnetic fields in the expansion region greatly enhances ion production. This electron injection configuration is used to generate both positive and negative cluster ions.

The resulting beam of cluster ions and accompanying neutrals is skimmed before entering the remaining part of the apparatus. Briefly, this consists of an ion optical beam line, an ExB mass separator (Wien filter) and a Faraday cup for ion detection. The Wien filter can be operated at a high electrostatic field where it achieves normal mass resolution over a limited mass range, or at a low electrostatic field where it exhibits poor resolution but over a much larger mass range. The latter mode is particularly useful for detecting very large cluster ions.

RESULTS

Lead cluster ions were generated under two different sets of source conditions. The first set employed a source aperture diameter of 1.0 mm, a helium pressure of 6.0 torr maintained at 195 K, and a crucible temperature of 1,460 K. Figure 1 presents mass spectra for both positive and negative lead cluster ions recorded under these conditions. In order to obtain these spectra, the Wien filter was operated in its high mass range mode. Both spectra exhibit a progression of unresolved cluster ion peaks ranging from $n \cong 40\text{-}400$ atoms per cluster ion, and for both ion polarities, the intensity maximum in the size distribution corresponds to $n \cong 200$. These lead cluster ions were estimated to range in diameter from $D \cong 15\text{-}30$ Å with the peak of the distribution at $D \cong 20$ Å. In the anion spectrum, an ion current of 600 pA at a beam energy of 1 keV was observed at this maximum. If average currents of

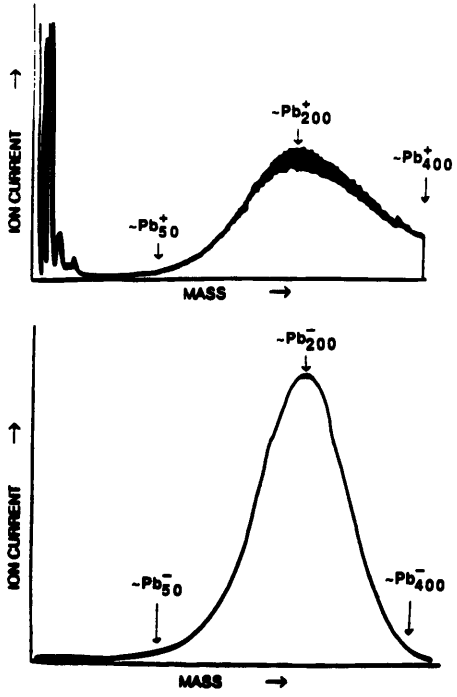

Figure 1. Mass spectra of large lead cluster cations (top) and anions (bottom) generated using the Smoke-Ion Source.

cluster anions are compared, this is over five orders of magnitude more intense than those available via laser vaporization techniques [17]. In the cation mass spectrum, a series of low mass peaks due to Pb^{++} and $Pb^{+}_{n=1-3}$ was observed in addition to the high mass distribution. Interestingly, these low mass peaks were absent in the anion spectrum, suggesting the small lead cluster cations may have resulted from fragmentation. The similarity between the high mass distributions in the cation and anion spectra may indicate that they reflect the neutral cluster distribution.

The second set of source conditions employed for lead cluster anion formation included a source aperture diameter of 1.5 mm, a helium pressure of 1.6 torr at 273 K, and a crucible temperature of 1,460 K. The resultant lead cluster anion mass spectrum was dominated by $(Pb)^{-}_{n=1-13}$, demonstrating the ability to shift the cluster ion size distribution by manipulating source conditions.

Cluster anions of lead sulfide were generated utilizing a 1.5 mm diameter source aperture, 3.7 torr of He at 273 K, and a crucible temperature of 1,265 K. Figure 2 shows the resultant mass spectrum of lead sulfide cluster anions $(PbS)^{-}_{n=2-7}$. Upon increasing the temperature of the crucible to 1320 K, $(PbS)^{-}_{n}$ anions extending in size to $n \cong 165$ ($D \cong 26$ Å) were observed in addition to the smaller cluster anions.

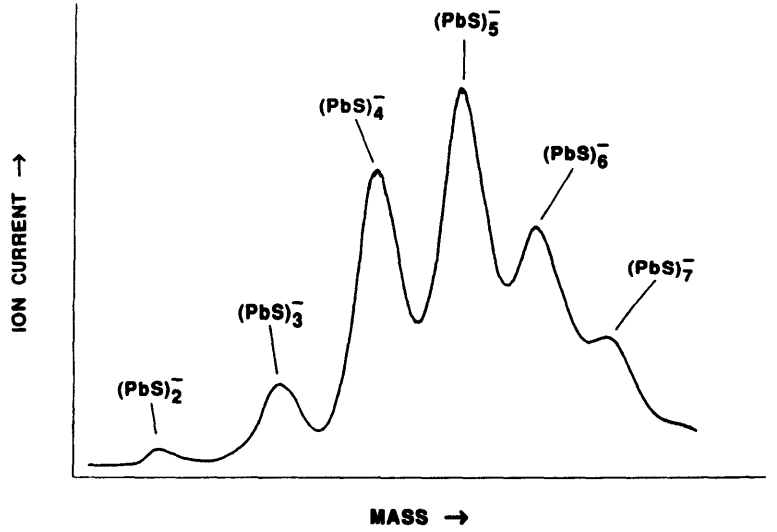

Figure 2. Mass spectrum of small lead sulfide cluster anions, $(PbS)^-_{n=2-7}$, generated using the Smoke-Ion Source.

Negatively and positively charged clusters of lithium were generated utilizing a 2.0 mm diameter source aperture, 1.5 torr of He at 273 K, and a crucible temperature of 1,100 K. This set of source conditions produced lithium cluster ion distributions that ranged from n≅650-2,800 (D≅30-50 Å). The intensity maximum in the distribution corresponded to n≅1,200 (D≅35 Å). Cluster anion currents as high as 1.25 nA at a beam energy of 500 eV have been observed at this maximum. By utilizing slightly higher He pressures in the condensation cell (3-5 torr), cluster anions comprised of 11,500 lithium atoms (D≅80 Å) have been generated.

Cluster anions of sodium were generated utilizing a 2.0 mm diameter source aperture, 1.9 torr of He at 273 K, and a crucible temperature of 785 K. A sodium cluster anion distribution that ranged from n≅700 (D≅35 Å) to well beyond n≅1,750 (D≅50 Å) was observed. The intensity maximum corresponded to n≅1,250 (D≅45 Å).

Magnesium cluster anions were generated utilizing a 2.0 mm diameter source aperture, 1.2 torr of He at 273 K, and a crucible temperature of 975 K. The resultant magnesium cluster anion distribution ranged from n≅150-850 (D≅20-35 Å), with the intensity maximum of the distribution at n≅375 (D≅25 Å).

Mixed lithium-magnesium cluster anions were generated by evaporating lithium and magnesium metals from separate chambers in a single crucible at a temperature of 1,015 K. Evaporation rates were controlled so that the ratio of Mg to Li atoms in precondensed metal vapor would be 3:1. Other source

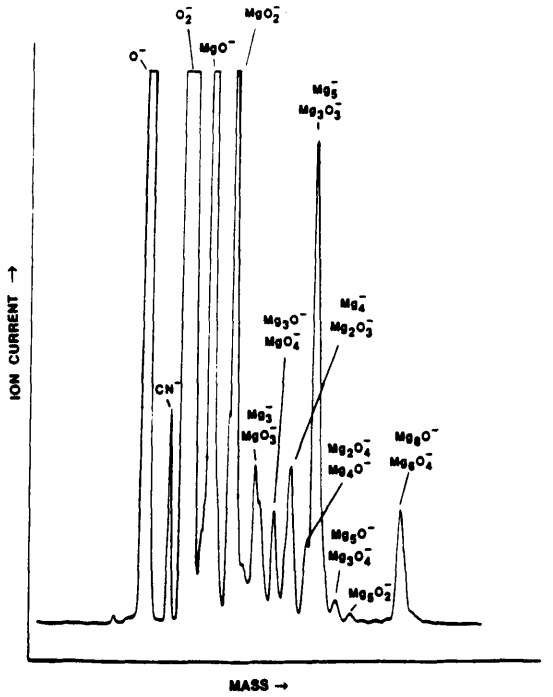

Figure 3. Mass spectrum of magnesium oxide cluster anions $(Mg_xO_y)^-$, as well as O_2^- and O^-, generated by adding a small amount of oxygen to the condensation cell of the Smoke-Ion Source.

conditions used included 1.2 torr of He maintained at 273 K and a 2.0 mm diameter source aperture. The $(Li_xMg_y)^-$ cluster anions observed ranged in mass from ~2,000-20,000 amu with the intensity maximum at ~7,000 amu. The ion current at this maximum measured ~1 nA at a beam energy of 500 eV.

Oxides of magnesium cluster anions, lithium cluster anions, and mixed lithium-magnesium cluster anions were generated under essentially the same source conditions used to generate pure and mixed metal cluster anions, but a small percentage of O_2 was added to the helium. For the formation of $(Mg_xO_y)^-$ anions, 1.0 % oxygen in helium was used in the condensation cell. The resultant mass spectrum, presented in Figure 3, shows peaks corresponding to $(Mg_xO_y)^-$ cluster anions of various stoichiometries along with O_2^- and O^-. In the case of the lithium-oxygen system, 1.5 % O_2 in helium was used. The resultant mass spectrum showed a series of unresolved $(Li_xO_y)^-$ cluster anions ranging in mass from 2,400-4,800 amu. Lithium-magnesium oxide cluster anions were also generated by using 1.5 % O_2 in helium, resulting in the formation of $(Li_xMg_yO_z)^-$ cluster anions ranging in mass from 1,300-9,000 amu. In all three cases, the addition of small amounts of oxygen to the condensation cell dramatically lowered the sizes of the particles produced in the source.

In a preliminary experiment, carbon cluster anions were generated in the Smoke-Ion Source using the "contact arc" method [18,19]. Total carbon cluster anion currents of several nanoamperes have been observed. In another preliminary experiment, nanoampere ion currents of cluster anions generated by evaporating sodium chloride were observed.

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