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Summary

A simple diode ion source has been developed for direct observation in a mass spectrometer of the positive ions created in an operating diode. The ionic species accelerated toward the cathode were identified. The shape of the peak displayed in the spectrum is related to the region of the diode in which the ions were formed.

Variation of experimental parameters, including the composition of the background gases, indicated that the characteristic shapes of the peaks can be related to space charge in the diode. This is complicated by the tendency of some of the species to fragment and further work is indicated before a complete understanding of the relations is obtained.

Alkali and halogen ions were observed when an emission current was drawn. These species are assumed to be present as anode impurities. Heavy bombardment of the cathode by alkali ions is associated with an apparent increase in cathode activity.

Heating an oxide cathode to temperatures as high as, or higher than, previous processing temperatures led to a further release of CO_2 from the cathode. This additional release was not observed with the conventional mass spectrometer ion source thereby indicating that important observations concerning the state of the cathode may be missed when the ions which are analyzed are not created within the operating diode.

INTRODUCTION

The residual atmosphere in an operating electronic diode provides neutral species that cross the region where electrons are being transported from cathode to anode. The operating voltages are usually high enough to provide sufficient energy to the electrons to cause electron impact ionization of the background species. Many studies involving selected species and both their positive ions[1-14] and negative ions[15-17] have been carried out. The work reported in this paper differs from the above in that the ions originating from different regions within the diode were observed in the same spectral scan. The diode was constructed so that the positive ions formed were accelerated toward the cathode, but rather than impacting on the cathode were injected into a mass spectrometer.

The relative behavior of selected ions from different regions was studied as a function of selected operating parameters of the diode as well as the composition of the background atmosphere.

EXPERIMENTAL

The experimental device shown in Fig. 1 was designed to be operated in the mass spectrometer as an independent ion source. This design permits operation of the conventional mass spectrometer ion source (CMSIS) so that normal mass spectrometer spectra can be obtained. It was placed in the chamber so that the positive ions produced when the diode is operated are accelerated toward the CMSIS and are focused on the entrance slit to the mass spectrometer. However, the spectrum from the diode source did not superpose that from the CMSIS because the diode-created ions were accelerated through a greater voltage after formation.

* Currently employed by Eagle-Picher Industries, Inc., Miami Research Laboratories, Miami, Oklahoma.
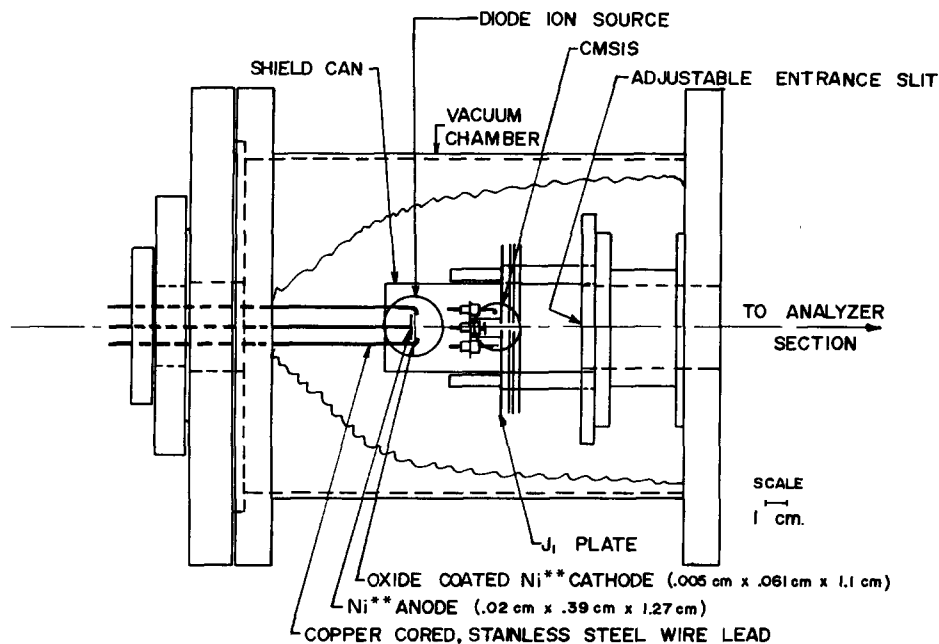
Fig. 1. The experimental diode and the mass spectrometer ion source (CMSIS) configuration.

The experimental device was installed in a 30.5 cm radius, 90° magnetic sector single focusing mass spectrometer*. The chamber housing the diode device was pumped by a 7.62 cm, three-stage, mercury diffusion pump with a liquid nitrogen cold trap and a thermo-electric chevron baffle, and was separated from the independently pumped flight tube region by a 0.005 in. slit. A background pressure in the low 10^{-7} Torr region was maintained during all experiments except those that involved bleeding in gases for identification purposes or for specific reaction studies.

Positive ions created in the interelectrode region by electron impact ionization were accelerated toward the cathode (a resistively heated, oxide-coated nickel** strip) by an interelectrode voltage drop normally maintained at 145 volts. A further drop of 90 volts between the cathode and the first plate (J_1) of the CMSIS was used to focus the ions on the analyzer section entrance slit. The above voltages were chosen to maximize the peak intensity for the ion of mass number 16. The electronic power supplies for the cathode and anode were floated at the mass spectrometer accelerating potential (normally 2500 volts).

A schematic diagram of the electronics is shown in Fig. 2.

The triple carbonate ($BaCO_3$ — 49 wt.%, $SrCO_3$ — 44 wt.%, $CaCO_3$ — 7 wt.%) used was

* Nuclide Corporation, State College, Pennsylvania.
** International Nickel Company; Alloy No. 271, Melt No. NP13A5HY, supplied by Somers Thin Strip Company.
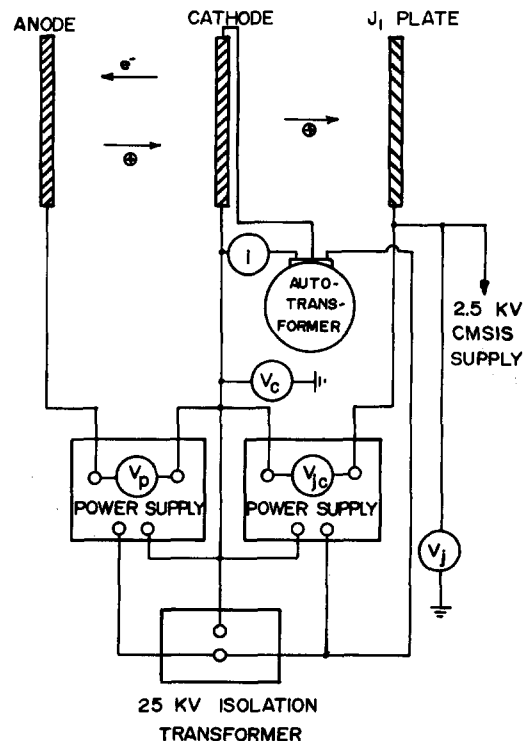

Fig. 2. Experimental arrangement for establishing the potential gradients to accelerate ions created in the diode ion source.

TABLE 1

Summary of CMSIS spectra related to cathode carbonate breakdown steps and diode spectra after cathode activation

| | CMSIS spectra | | Diode spectra | |
Temperature	Observation	Remarks	Observation	Remarks
200	Start cathode	H_2O neutral		
300	outgassing	precursor		
400	Second major	H_2O neutral		
500	cathode outgassing	precursor; mass		
600		30 ion (binder)		
700	Start cathode	CO_2 neutral		
800	carbonate decomposition	precursor		
900				
1000				
1100	End cathode decomposition,		Emission current	Characteristic of
1200	residual MS atmosphere		observed	(1) anode region
				Na^+, K^+, F^+, Cl^+, O^+;
1300	Cathode material	BaO^+ observed		(2) interelectrode
1400	transport observed			region, CO^+, O_2^+, CO_2^+

provided by Western Electric Co.*. The gases used for identification and reaction studies were of industrial purity.

The cathode temperature could not be measured directly with the diode ion source mounted in the mass spectrometer. Therefore, the ion source was mounted in a separate vacuum system and a calibration curve was prepared relating filament heating current to filament temperature. A cross check was made by comparing the temperature obtained via an optical pyrometer with that obtained from a platinum/platinum—10% rhodium thermocouple spot welded to the filament. The temperatures obtained were consistent and reproducible within 20 deg C.

RESULTS AND DISCUSSION

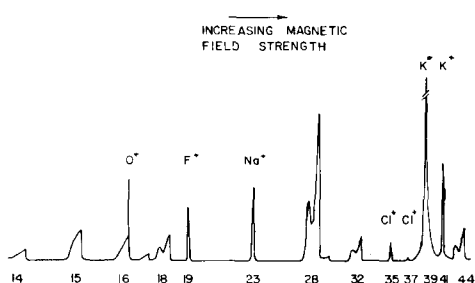In order to obtain a spectrum from ions formed in the diode, the cathode must be an

Fig. 3. Tracing of a diode mass spectrum.

active electron emitter. Therefore, until the cathode was activated, the breakdown of the carbonate coating was followed by spectra taken with the CMSIS.

The decomposition of the cathode carbonate coating established a uniform pattern for all of the cathodes used in this study. A summary of the major events in the cathode activation and the major gaseous species observed is given in Table 1.

When an emission current in the diode could be obtained, the electron beam in the CMSIS was shut off and a mass spectrum of the ions formed in the operating diode was produced. Table 1 gives a summary of the major ions observed in the diode spectra compared with the activation steps. A reproduction from an actual diode spectrum is shown in Fig. 3.

Some of the peaks look like normal mass spectrometer output (see 19, 23, 35, 39 and 41 on Fig. 3), that is, the peaks are narrow and symmetrical in shape. This type of peak will be referred to as a spiked peak. Such spiked peaks are characteristic of ions created in a uniform potential region. In the diode device the potential varies in the interelectrode region, hence only ions formed on or very near the cathode or anode would be formed in a region of essentially uniform potential.

The second type of peak has two distinct forms but is characterized in general by a broad, asymmetrical shape. One form has a uniformly increasing intensity with a single maximum at the high mass edge of the peak

(see 14, 15 and 17 in Fig. 3).

The other form has a maximum not only at the high mass edge, but also at the low mass edge (see 18, 28, 32 and 44 on Fig. 3).

If each broad peak is assumed to correspond to ions of a single mass, then these ions appear dispersed in mass because they were accelerated through different potentials and hence have different kinetic energies. Ions created at different locations in the potential gradient between the cathode and anode would have such a spread in energy. The edges of the peak represent the limits of the spread in energy of the ions; therefore, the edges of the peaks should be related to the cathode and anode potentials. Calculations using the mass spectrometer focusing equation, $m/q = R^2 B^2/2V$, where m = mass of the particle in kg, V = total accelerating voltage experienced by the ion in volts, R = radius of path in m, q = charge on the particle in C, and B = magnetic field strength in wb/m^2, indicate that the ions corresponding to the low magnetic field strength edge were created at the lower potential. From this it can be assumed that the ions contributing to the left edge (low magnetic field strength) of an asymmetric peak were created in the cathode region while those contributing to the right edge were created near the anode region. Because the electrons that impact with the neutral species must acquire sufficient energy from the interelectrode field to cause ionization, the spread in the peak that can be calculated in terms of the accelerating voltage is less than the impressed potential drop of 145V. N^+ was used as a reference and gave a peak spread of 110 V.

This analysis is confirmed by the only peak in the spectrum that combines both a spiked and dispersed shape, specifically 16 in Fig. 3. Peak 16 has a uniformly increasing intensity characteristic on ions being formed in the interelectrode region, and terminates in a spike that is characteristic of ions formed on (or very near to) the anode. A careful indexing by calculation of all peaks, starting from the anode side, confirmed the chemical assignments. In addition, several gases (CO_2, O_2 and Ar) were admitted to the ionization region and used to confirm further the indexing assignments. In those cases where the isotope structure could be observed (Cl and K), these additional data confirmed the assignments.

The spiked peak spectrum was used to identify the following ions; O^+, F^+, Cl^+, Na^+ and K^+. In some cases, an indication of Rb^+ was observed also. All of these species were characterized as originating on the anode of the operating diode via what appears to be a combination of heating of the anode by radiation and by electron bombardment from the cathode. When these species were observed in a diode spectrum, a switch to the conventional ion source gave a spectrum that did not contain these species.

The peaks attributed to the halogens were observed over a wide range of operating conditions. These peaks increased in height relative to the asymmetrical peaks as the emission current was increased either by increasing the cathode temperature or increasing V_p at constant temperature. The halogen peaks were observed at lower current densities than were the alkali peaks.

The spikes attributed to the alkali metals were not always observed along with the halogen ions. Their appearance was more effectively initiated by drawing an emission current than by increasing the cathode temperature. The spectrum of Fig. 3 was taken at a time when the amount of alkali emission from the diode was particularly large. The relative intensity of the alkali spikes increased to the proportions shown in Fig. 3 when an emission current of 16 mA was obtained at a V_p of 145 V. This represents a current density of 61.5 mA/cm^2 at the cathode surface, and 32 mA/cm^2 at the anode surface. Lower values of the emission current were relatively ineffective in generating alkali ions at this cathode temperature ($1200°C$). The appearance of the alkali spikes was accompanied by an increase in emission current for a constant applied voltage. In one case, as V_p was increased to 145 V, the emission current followed the voltage increase and reached 16.0 mA at 145 V; however, it continued to rise to 17.2 mA while V_p remained constant. After a few seconds the emission current decreased to about 16.0 mA. Subsequent spectra did not exhibit alkali peaks as high as those exhibited in the spectrum shown in Fig. 3. The increase in emission current at constant V_p can be taken as evidence of a change in cathode activity. The correlation between alkali peak appearance and the change in activity suggests that the alkali ions lowered the external work function of the cathode during the period of

TABLE 2
Summary of changes in diode spectra induced by variation in diode conditions or residual atmosphere

Parameter changed	Parameters held constant*	Changes in diode operation	Observed changes in peak for ion with $m/q = 28$		Anode/cathode intensity		Remarks
			In relative ion intensity from cathode region	In relative ion intensity from anode region	Before change	After change	
Filament temperature lowered 1060° to 1000°C	a and b	Emission current dropped 57%; 7 mA to 3 mA	Decreased 30%	Decreased 60%	3.16	1.80	
Anode to cathode voltage increased 105 V to 150 V	b and c	Emission current constant	Increased 250%	Decreased 3%	3.33	0.93	
CO_2 (g) admitted background pressure 3.9×10^{-7} to 7.6×10^{-7} Torr	a, b and c	Emission current dropped 27%; 11 mA to 8 mA	Increased 195%	Increased 2.5%	4.45	1.62	Peaks at 17, 18, 28, 32 and 44 increased; Mass 44 ion (CO_2^+) increased 330%
Ar (g) admitted background pressure 3.7×10^{-7} to 8.0×10^{-7} Torr	a, b and c	Emission current dropped 18%; 5.5 mA to 4.5 mA	Increased 425%	Increased 5%	12.7	2.53	Peaks at 18,28 32, 40 and 44 increased

* a. Anode-to-cathode voltage   b. Cathode-to-CMSIS voltage   c. Cathode temperature
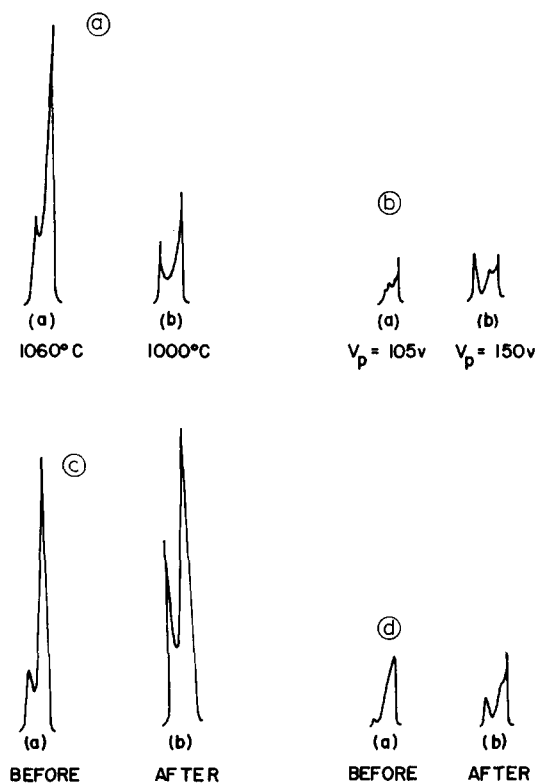
Fig. 4. Peak shape changes (for mass 28) resulting from variation of selected operating parameters (relative intensity scale constant). a. The effect of lowering the cathode temperature; b. The effect of increasing V_p; c. The effect of CO_2 admission; d. The effect of argon admission.

greater bombardment leading to a more active cathode.

It appears that the anode metal itself contains the alkalis and halogens as impurities. Further work is being carried out to establish the level of sensitivity of this technique for these specific impurities.

It was observed during the study that the dispersed peaks with double maxima underwent large changes in the relative heights of the two maxima as operating parameters were changed. The major observations are summarized in Table 2. Figure 4 shows schematically how the spectrum peaks changed and the relative intensities from spectrum to spectrum.

The following observations were made using Table 2. 1. There is a large increase in the number of ions created at the cathode when either CO_2 or Ar is admitted, or the anode-to-cathode voltage is increased. At the same time, the number of ions created at the anode remains essentially constant. The increase in the number of ions at the cathode

occurs even though in two cases the electron current dropped significantly. In all cases the ratio of ions created at the cathode to ions created at the anode increased with the changes made in operating parameters. Other peaks in the spectrum were observed to change shape and height along with those of the admitted gases. 2. A doubling of the background pressure, as measured by a separate ion gauge, appeared to result in a 30-fold increase in ion concentration near the cathode as observed via peak intensity.

The above observations suggest that small changes in electron emission can be detected and followed through the positive ion spectrum. Further experimentation is being carried out to establish whether the electron emission from the cathode is being affected directly or whether space charge buildup is the important factor.

The peaks at m/q of 18, 28, 32 and 44 exhibit a tendency to produce two maxima while the peaks at m/q of 12, 14 and 16 tend to form only a single maximum. The peaks at m/q of 18, 28, 32 and 44 are due to ions of H_2O^+, CO^+, O_2^+ and CO_2^+ respectively which are subject to fragmentation during collision with electrons emitted in the experimental diode. The peaks at m/q's of 12, 14 and 16 are due to the monatomic species C^+, N^+ and O^+ respectively and further fragmentation is not possible.

If a molecule of CO_2 is struck by an electron and simple ionization takes place, eqn. (1) describes the process.

$$CO_2(g) + e^- \rightarrow CO_2^+ + 2e^-. \quad (1)$$
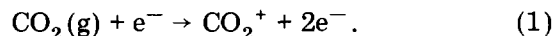
If the electron has sufficient energy, a process of the type shown in eqn. (2) may occur.

$$CO_2(g) + e^- \rightarrow CO^+ + O + 2e^-. \quad (2)$$
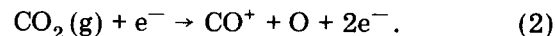
If this occurs, the CO_2 molecule which could have contributed to the mass number 44 peak is lost via fragmentation. Different types of fragmentation processes produce different species and the energy required varies among processes. The asymmetrical peaks observed from the experimental diode can be thought of as a plot of the relative number of ions reaching the detector versus energy at creation. The relative height of the peaks of m/q of 28, 32 and 44 might be lowered at

TABLE 3
Cathode outgassing behavior during thermal cycling

Cathode operating conditions	Relative intensities for I^+_{44}/I^+_{14}		Emission current
	Diode source	CMSIS	
Cathode temp. raised to 1160°C after 34 min at 1125°	1.38		14 mA
Cathode temp. lowered to 1100°	0.66	No change observed from 1160° operation	3 mA
Cathode temp. raised to 1160°	0.96	No change observed from 1100° operation	8 mA

points along the energy distribution corresponding to processes in which fragmentation occurs.

Further work is being carried out to determine if this technique can produce data leading to a separation of simply ionized species and fragments in a complicated spectrum.

As has been noted above, the diode spectra were more sensitive to changes in diode atmosphere than were the CMSIS spectra. One case, involving outgassing of the cathode at high temperatures, is summarized in Table 3. These data indicate, as has been noted before by others[18], that raising an oxide cathode to a temperature higher than its previous operating or processing temperature can result in further outgassing, with CO_2 as the principal species.

Oxide materials may be transported by evaporation, by positive ion bombardment, or by a combination of these mechanisms. In the present investigation nondispersive X-ray analysis of the anode in a scanning electron microscope revealed the transport of Ba and Sr at a cathode temperature of 1250°C. At a cathode temperature of 1370°C the presence of BaO^+ was observed in the CMSIS spectrum and spherical globules were subsequently observed on the anode surface. Calcium was not detected using non-dispersive X-ray analysis and neither SrO^+ nor CaO^+ was observed in any CMSIS spectra.

CONCLUSIONS

In the present investigation positive ions

created during the operation of a simple electronic diode were sampled and analyzed by mass spectrometry. The ionic species accelerated toward the cathode were identified and their region of formation was related to the shape of the mass spectrometer peak. Changes in the shape of the peaks corresponding to ions created in the interelectrode space appear to be correlated with changes in the space charge existing in the cathode region. A decrease in the amount of space charge led to an increase in the height of the peak maximum which corresponded to ions created in the cathode region. This technique appears to be very sensitive to changes in the state of the diode.

Alkali and halogen ions were released from the anode when an emission current was drawn. Heavy bombardment of the cathode by alkali ions was associated with an apparent increase in cathode activity. The increase in activity was attributed to a lowering of the external work function by the alkali ions.

Heating an oxide cathode to a temperature higher than the previous operating temperature led to further release of CO_2 This could lead to significant changes in cathode activity in a sealed electronic tube.

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