

Ion Formation in Field Desorption of Salts

F. W. Röllgen, U. Giessmann, and H. J. Heinen

Institut für Physikalische Chemie der Universität Bonn

(Z. Naturforsch. 31 a, 1729–1730 [1976];
received October 22, 1976)

It is shown that field emission of cations from adsorption layers of salts results from an ionic conductivity of the salt layers.

In field desorption (FD) mass spectrometry of inorganic and organic salts a high emission of cations and clusterions is already observed at field strengths which are insufficient for the ionization of organic molecules ($<10^7$ V/cm)^{1–5}. In addition it is found that the field strength for the onset of emission of cations falls with rising anode temperature. These phenomena were originally explained as due to surface reactions similar to those assumed for the thermal surface ionization of alkali halides³. More detailed investigations of the FD of LiJ and $(C_2H_5)_4NJ$ from non activated 10 μ m tungsten wires showed, however, that the desorption of the cations takes place via a mechanism based on an ionic conduction in the salt layers.

This result stems from the observation that the energy deficit of the cations relative to the anode potential is always larger at the beginning of the desorption process than at the end when the reservoir of the substance on the surface of the emitter is exhausted. The reduction of the energy deficit corresponds to a decrease in the appearance potential of the cations. In most cases the energy shift is several volts, and is observable in single focusing magnetic mass spectrometers in the shifting and broadening of ion signals on the mass scale. Since these differences in the energy deficit can only be attributed to a varying potential drop across the adsorbate layer it follows that the ion emission does not take place from regions of the surface with low adsorbate coverages, as previously assumed, but from areas of high coverage. Electron micrographs show that the thickness of the adsorption layers can achieve several micrometers.

For ion emission from thick salt layers the question of the mechanism of charge transport through the layers arises. In the case of the alkali halides, which are not electronic but typical ionic conductors⁶, an ionic conduction mechanism by diffusion of lattice vacancies has to be assumed. However, such an ionic conduction mechanism must

also exist in the case of the ammonium salts and most organic and inorganic salts as well, since these show similar desorption behavior to the alkali halides.

The phenomena observed during FD of salts can be explained by the thermally activated ionic conduction of the salt layers. At sufficiently high temperatures the high electric field induces a charge separation in the adsorption layer which leads to a charging of the surface of the salt layer with cations. The negative charges are assumed to be transferred to the tungsten wire accompanied by chemical reactions taking place at the phase boundary metal/salt. In the case of lithium iodide J_2 or metal iodide may be formed. The conductivity of LiJ, which is a cation conductor⁶, is principally determined by the diffusion of Schottky-defects. The activation energy for the diffusion of these defects is only 0.38 eV⁷. It is thus possible that a field-induced charging of the salt layer with Li^+ ions takes place even at room temperature, and indeed a Li^+ emission is observable at this low temperature.

However, the FD of salts does not depend only on the ionic conductivity but also on the work function of the cation, that is the energy necessary to transfer the cation from the solid to the gas phase. This work function depends on the charge state of the surface and on the crystal lattice energy of the salts. The latter may explain for example why the thermal activation for the desorption of $(C_2H_5)_4N^+$ ions from a $(C_2H_5)_4NJ$ adsorption layer is lower than that for the removal of Li^+ ions from LiJ. The typical bursts of emission observed during the FD of salts at low temperatures can be attributed to space charge effects i.e. to the desorption of a part of a surface layer on exceeding a critical charge density, since it is probable that the thermal activation of cations is not sufficient to overcome the work function under these conditions.

An important aspect of the problem is the energetics of the desorption of ions. Three contributions to the energetics of cation formation can be distinguished: 1. charge transport by ionic conduction, 2. electron transition at the phase boundary salt/metal, 3. desorption of the cation. The appearance potential (AP) of field ions depends on the energetics of ion formation⁸. However, in measuring such appearance potentials only those energy contributions which produce a potential deficit between the emitter potential and that at the place of formation of the ions are included. The AP of Li^+ ions desorbing at ca. 400 °C from a LiJ adsorption layer on tungsten was found to be 8.0 ± 0.5 eV, using a method given in Reference⁹. An AP equal to the ionization potential (IP) of lithium is only to be

Reprint requests to Prof. Dr. F. W. Röllgen, Institut für Physikalische Chemie der Universität Bonn, Wegelerstraße 12, D-5300 Bonn.

expected if the electron acceptor level of the Li^+ ions at the point of desorption were in resonance with the Fermi-level of the metal emitter. However, this state cannot be achieved since the Li^+ ion emission leads to additional potential drops at the phase boundary metal/salt and across the salt layer. These potential drops and therefore also the APs are temperature dependent and decrease with rising emitter temperatures. The measured APs were, however, always noticeably larger than the IP of lithium.

In closing it may be pointed out that cation emission from ionic conductors represents a new phenomenon in field emission. From the electrochemical point of view this is a single electrode system with a solid electrolyte.

Acknowledgement

This work is sponsored by the Deutsche Forschungsgemeinschaft and the Fonds der Deutschen Chemischen Industrie.

¹ F. W. Röllgen and H.-R. Schulten, *Org. Mass Spectrom.* **10**, 660 [1975].

² H.-R. Schulten and F. W. Röllgen, *Angew. Chem.* **87**, 544 [1975]; *Int. Ed.* **14**, 561 [1975].

³ F. W. Röllgen and H.-R. Schulten, *Z. Naturforsch.* **30 a**, 1685 [1975].

⁴ U. Giessmann and F. W. Röllgen, *Org. Mass Spectrom.* **11**, 1094 [1976].

³⁵ F. W. Röllgen, U. Giessmann, H. J. Heinen, and S. J. Reddy, *Int. J. Mass Spectrom. Ion Phys.*, in press.

⁶ L. W. Barr and A. B. Lidiard, in *Physical Chemistry — An Advanced Treatise*, Vol. X, Solid State (ed. W. Jost), p. 151, Academic Press, New York 1970.

⁷ Y. Haven, *Rec. Trav. Chim.* **69**, 1365 [1950].

⁸ H. J. Heinen, F. W. Röllgen, and H. D. Beckey, *Z. Naturforsch.* **29 a**, 773 [1974].

⁹ H. J. Heinen, H. H. Gierlich, and H. D. Beckey, *J. Phys. E* **8**, 877 [1975].