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Common principles of Ba and Th dispenser cathodes for high emission applications

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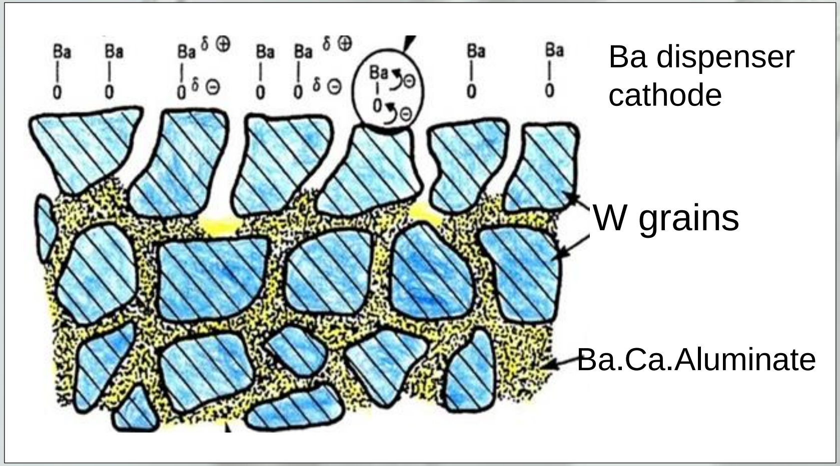
Common principles of Ba and Th dispenser cathodes for high emission applications

Outline:

1. Common features of mono-layer dispenser cathodes
2. High emission capability and applications of
   a) Ba and Ba Scandate dispenser cathodes
   b) Th and La dispenser cathodes
3. Surface analysis results for Ba dispenser cathodes, emission model and Ba supply mechanisms
4. Surface analysis results for Ba scandate dispenser cathodes and emission model
5. Surface analysis results for Th dispenser cathodes and Th supply mechanisms
6. Other types of dispenser cathodes
7. Discussion and conclusions

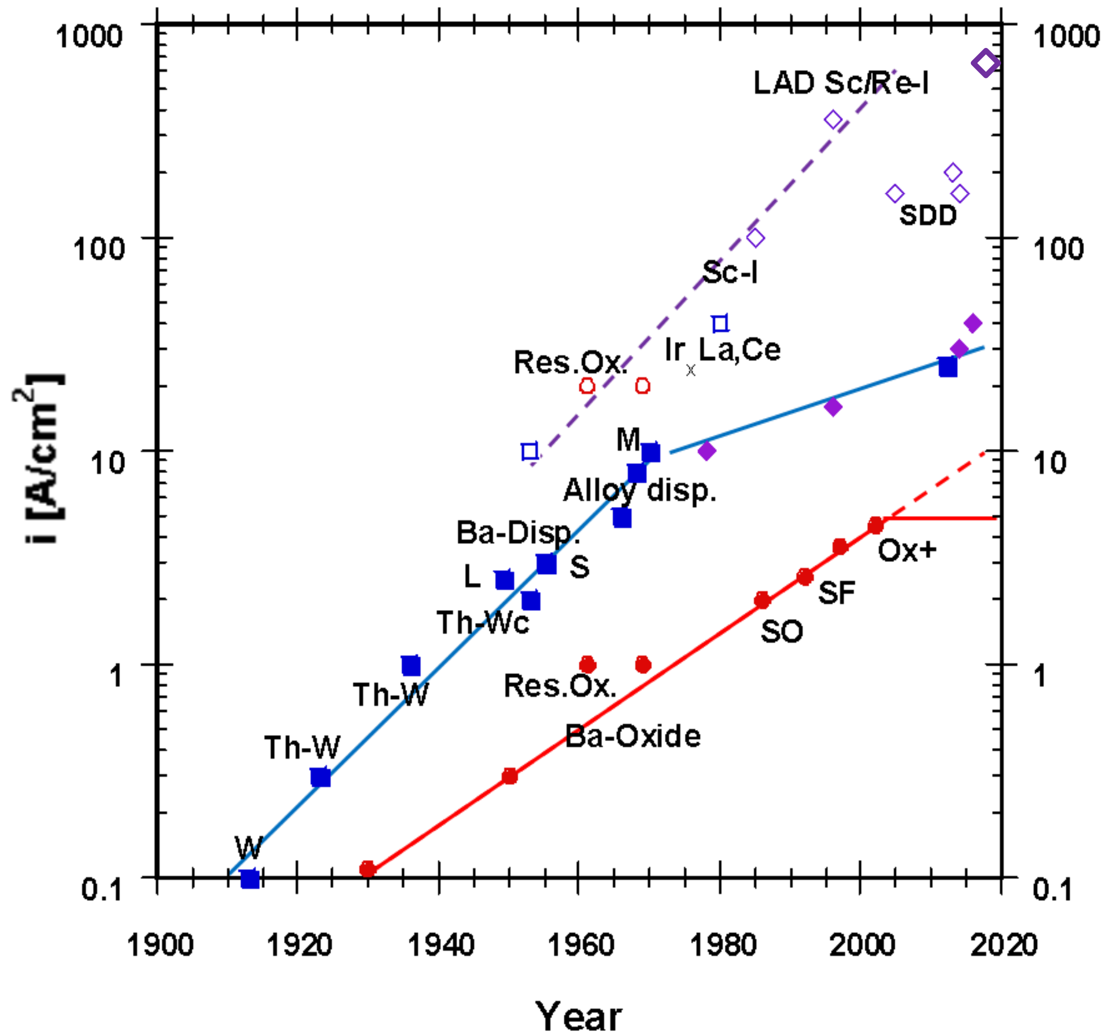
1. Common features of dispenser cathodes

Nearly all successful types of thermionic cathodes such as impregnated Ba cathodes, Ba scandate cathodes, thoriated tungsten or lanthanated molybdenum cathodes are dispenser cathodes (in German: "Nachlieferungs-kathoden"), which rely on the continuous supply of a monoatomic surface layer consisting of Ba, Th, La or another low work function metal.
Usually the work function of the surface layer is further reduced by the specific bound surface state, e. g. via a subtractive dipole moment [1].



For formation and compensation of losses by evaporation and ion bombardment the emissive atoms of the surface monolayer need to be generated and replenished e.g. via a chemical reaction of a source compound (in the cathode matrix, in the pores, or in a separate reservoir) with the base matrix at elevated temperatures. The low work function metal atoms then diffuse to the surface and spread over it. In the following we will discuss it in detail for the cathode types addressed [1,2].

2a) Progress in cathode performance over time



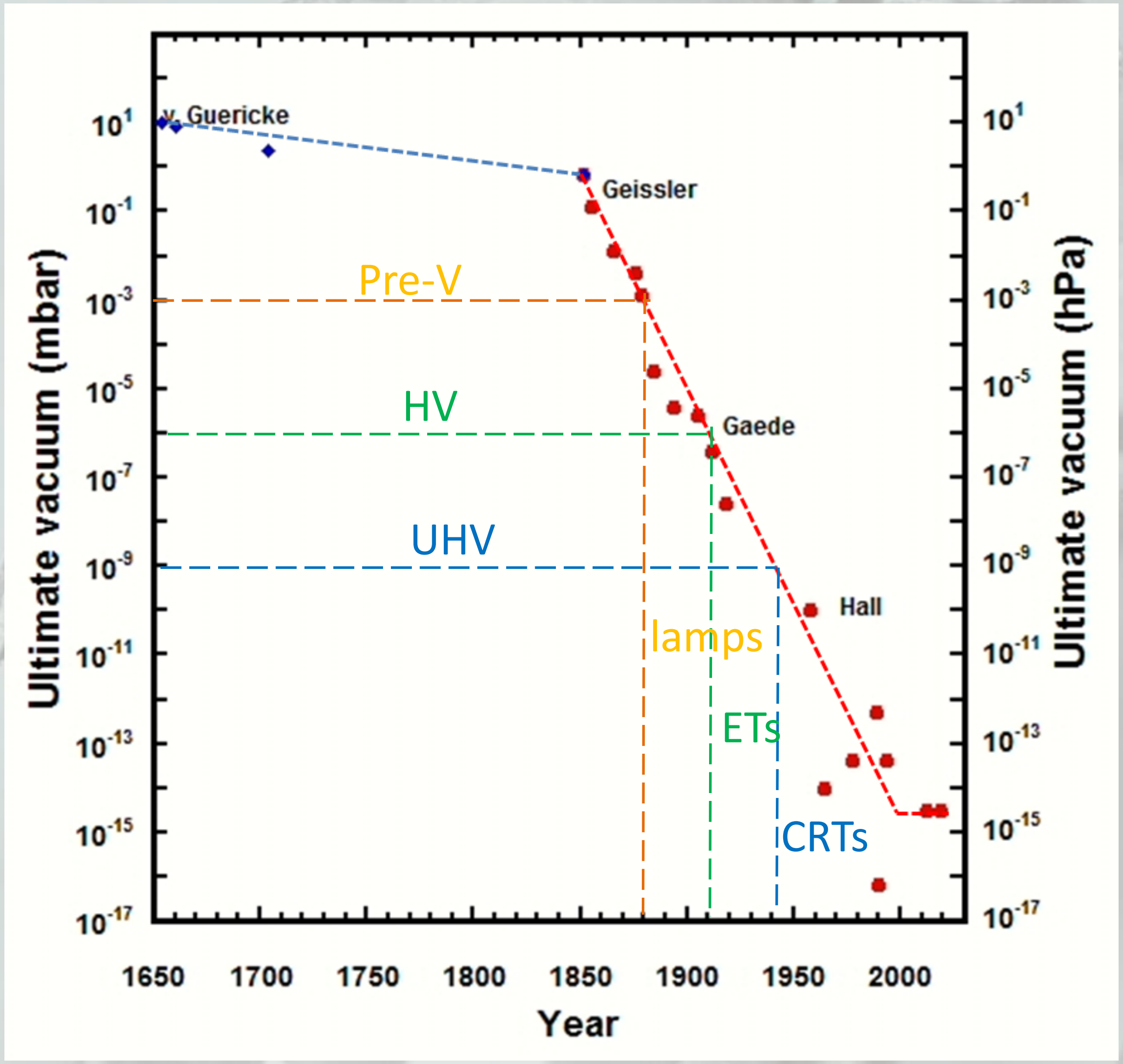
(Copyright Georg Gaertner, Aachen, Germany)

Historical development of thermionic cathode emission capabilities - an update.
The lower red line : dc emission of oxide cathodes (red circles). The upper blue line: metal matrix based (including Ba dispenser) cathodes; Scandate cathodes: violet diamonds.
Open symbols + dashed line: pulsed emission data including Scandate cathodes.

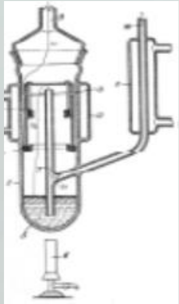
It illustrates the high emission capability of Scandate cathodes [2-6]

Current top result 670 A/cm^2 pulsed 20 Hz, 5 µs, T = 1100°C$_b$ of S. Yin 2020 [6]

2b) Cathode progress (and tube types) are linked to improvement in vacuum techniques



Ultimate vacuum achieved versus time, see [3].

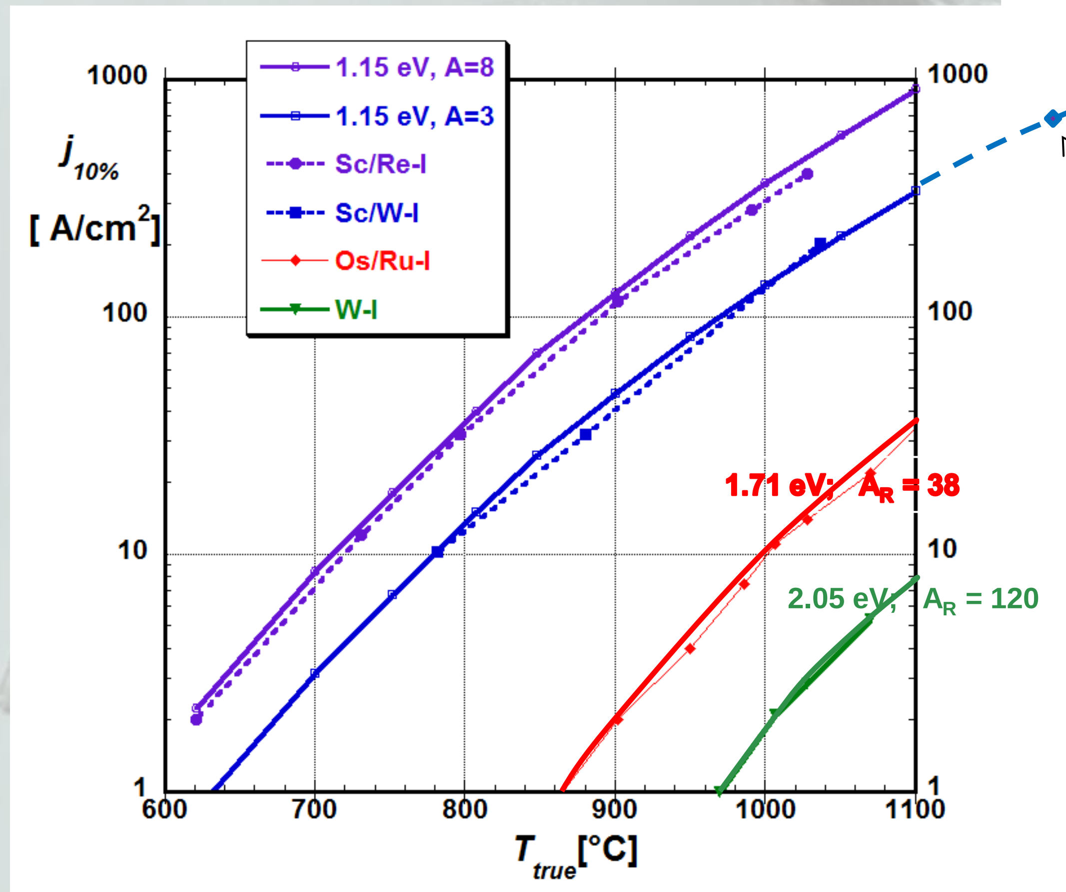


Hg diffusion pump Gaede 1915

Balzers turbomolecular pump (Becker 1958)

Varian ion getter pump (Hall 1958)

2c) Saturation emission current density $j_s \approx j_{10\%}$ versus true temperature of Ba and Ba scandate dispenser cathodes



Violet curves: LAD with Re (on W-I): in short: Sc/Re-I

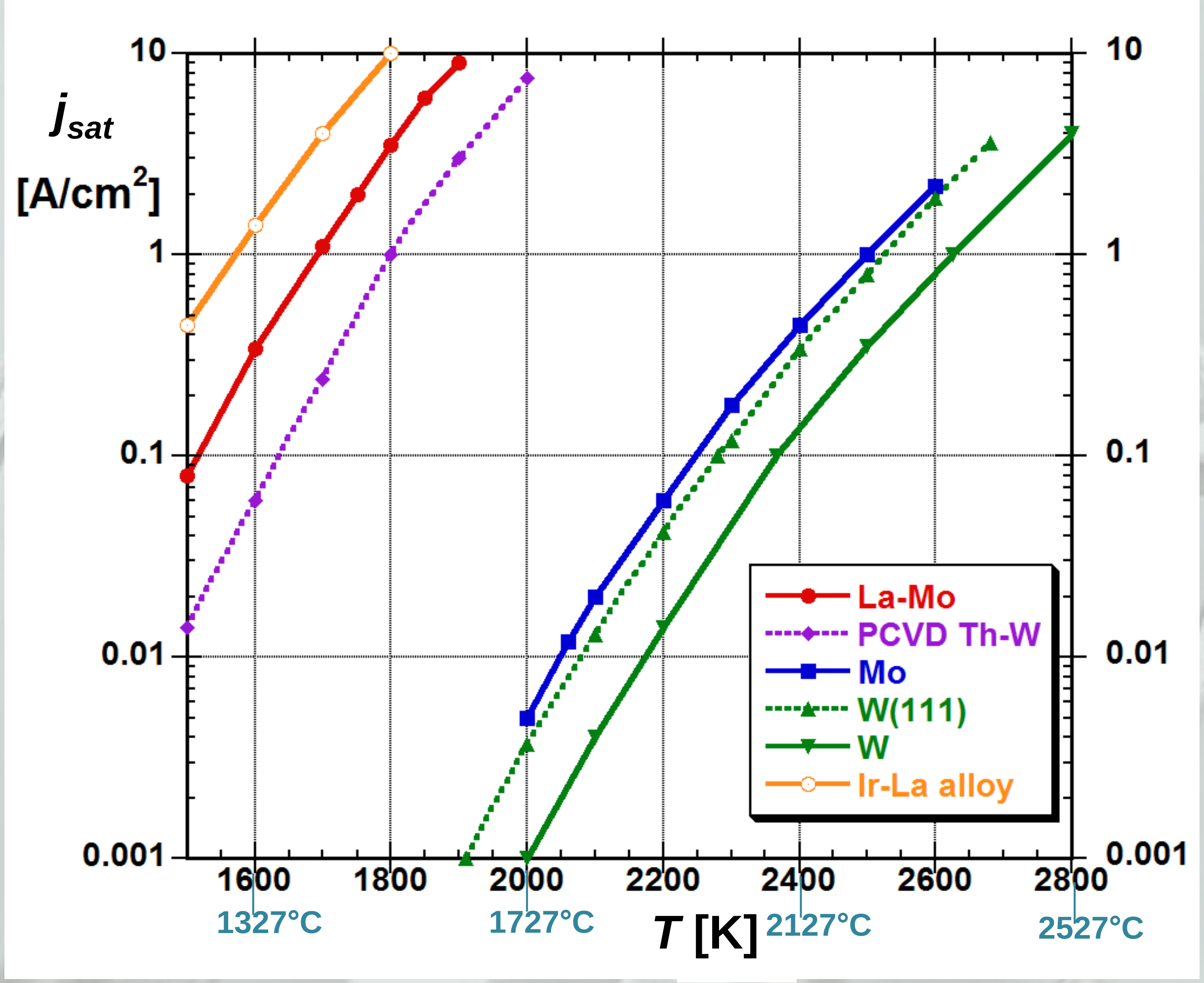
Blue curves: Sc/W-I

The blue (check) data point outside the scale is the top result of Shengyi Yin from 2020, compatible with W and A_R = 3 at about 1190 °C true temperature [6]

The dimension of A_R is $A/(cm^2K^2)$

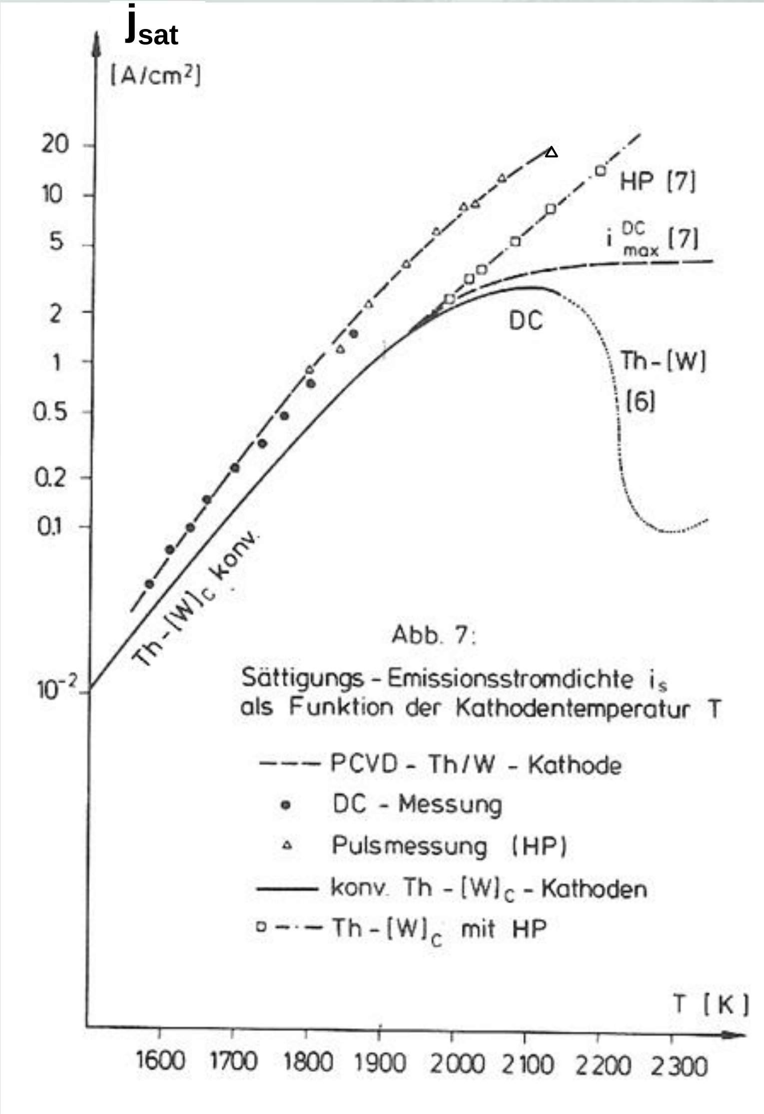
A general feature of all Ba-scandate cathodes prepared by LAD or other methods is the **work function** of about **1.15 eV** (also determined by FERP), whereas the Richardson constant A_R is varying between 3 and 8 $A/(cm^2K^2)$. For Os/Ru-I cathodes 1.71 eV and A_R = 38 $A/(cm^2K^2)$ and for W-I cathodes 2.05 eV and A_R = 120 $A/(cm^2K^2)$ give a good fit [2].

2d. Emission current density of metal, metal alloy and Th and La dispenser cathodes as a function of true temperature



Data are based on G. Gaertner, H. Koops, "Vacuum Electron Sources and their Materials and Technologies", chapter 10 of *Vacuum Electronics, Components and Devices*, Ed. J. Eichmeier, M. Thumm, Springer 2008 [1] and on B. Djubua et al. [14] and I. Weissman [1]. Copyright Georg Gaertner, Aachen, Germany, 2020; See also Fig. 5.22 in "Modern Developments in Vacuum Electron Sources" [2]

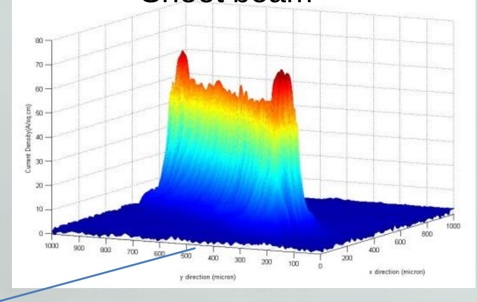
2e. Saturated emission current density i_{sat} of different types of thoriated tungsten cathodes as a function of temperature T



Typically the carburized thoriated tungsten wire cathodes as known from literature before 1980 (Th-[W]c) show an emission decline at temperatures above 2100 K. This must have been due to non-ideal vacuum conditions, since we did not observe it for the same cathodes at dc load in UHV. Moreover we found a further increase in this region with pulsed emission.
The Th/W cathodes prepared by Plasma-activated CVD (Chemical vapor deposition) by Philips showed a significantly higher emission due to an increased Th surface coverage as proven by an increased Richardson constant!

The figure is from ITG Fachtagung Elektronen-röhren und Displays 1989, Fachbericht 108, Garmisch-Partenkirchen, presented by G. Gärtner et al. [11]. The highest j_{sat} was 20 A/cm² pulsed, the highest j was 30 A/cm² pulsed. These are the best values achieved with thoriated tungsten !

2f. Application areas:


Sheet beam

Comparison of emission capabilities of dispenser cathodes :

The lower their work function → the lower the temperature range!

The highest emission exhibit Ba Scandate dispenser cathodes, pulsed emission 300 A/cm^2 at 1000 °C ; dc emission 15 to 75 A/cm^2.

Main application areas are in TeraHertz imaging and in Gyrotrons [1-5].

At the same temperature Os/Ru-I cathodes reach 10 A/cm^2 dc and pulsed, and W-I reach 3 A/cm^2, but can also be applied at higher temperatures. Their main application is in RF and microwave tubes, especially for long life satellite transmission [2].

Th (and La) dispenser cathodes have been mainly used in rf tubes, but at operating temperatures around 1750 °C. A potential new application is in micro-fusion reactors (→D. Velazquez et al. (Avalanche Energy) O-019, IVESC 2023, [12]). The higher temperature implies a higher heating power, but increased temperature has the advantage of higher robustness versus gas poisoning. This is the reason, why in X-ray tubes with the worst rest gas pressures still pure tungsten cathodes without monolayer films are used.

3. Surface analysis results for Ba dispenser cathodes and Ba supply mechanisms

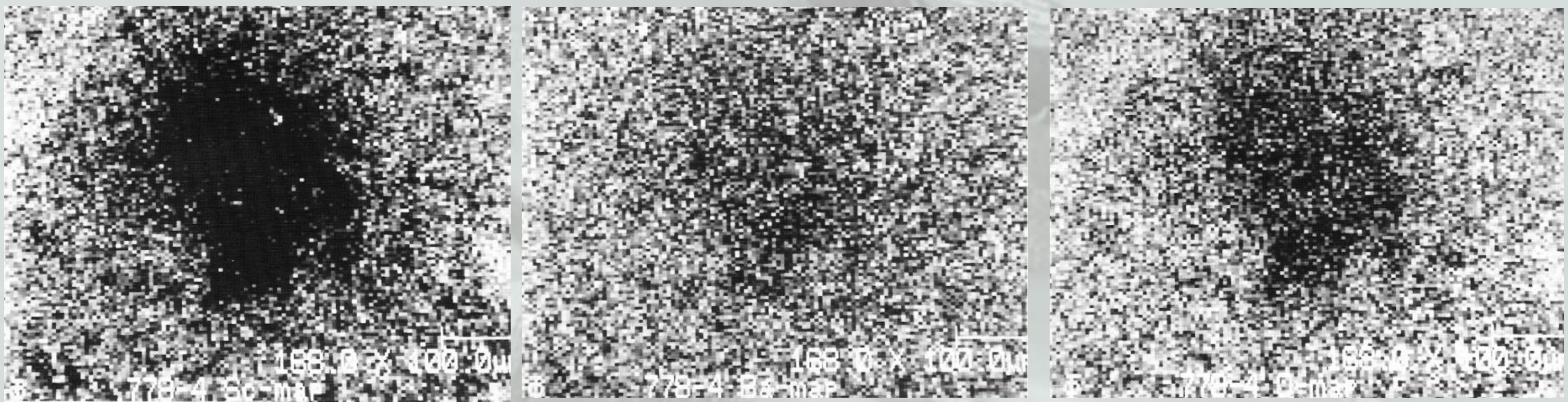
From high resolution surface characterization by several methods the existence of a mono-atomic Ba surface layer has been proven:

a) **The first method of choice is Auger Electron Spectroscopy (AES), which is sensitive for about 1nm surface depth; the removal of the monolayer by excessive heating or ion sputtering can also be detected, especially by Scanning Auger Microscopy (SAM)**

b) **A second method sensitive for about 1 mono-atomic layer is Low Energy Ion Scattering (LEIS) with He^+, Ne^+ or Ar^+ ions, which was used for Ba dispenser cathode surface characterization by R. Cortenraad et al. [8]**

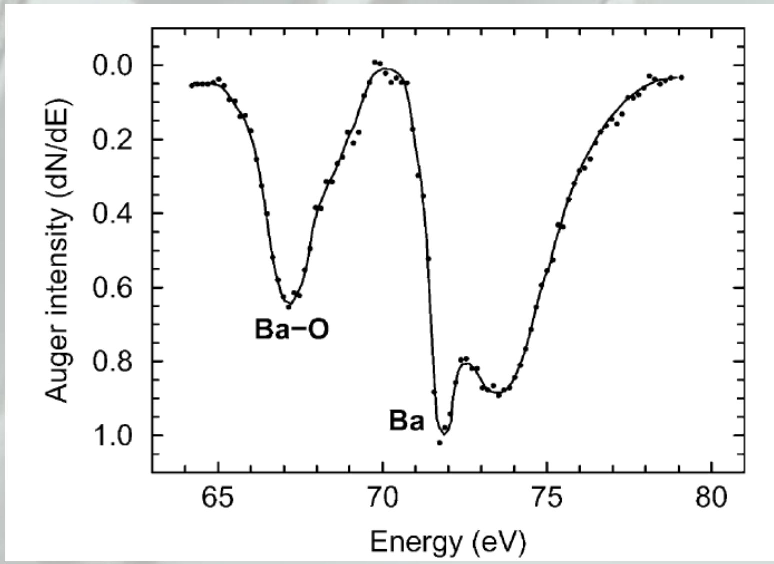
c) **Determination of Ba diffusion length on the surface by indirect methods: This was done e. g. by B. Free and R. Gibson in 1985 by using a ribbon with either slit or holes in between cathode and anode and measuring the steady state electron current from the ribbon surface under space charge limited conditions. They obtained a Ba diffusion length of about 80 µm at 1100 °C [7]**

3.1 Surface analysis results for Ba dispenser cathodes

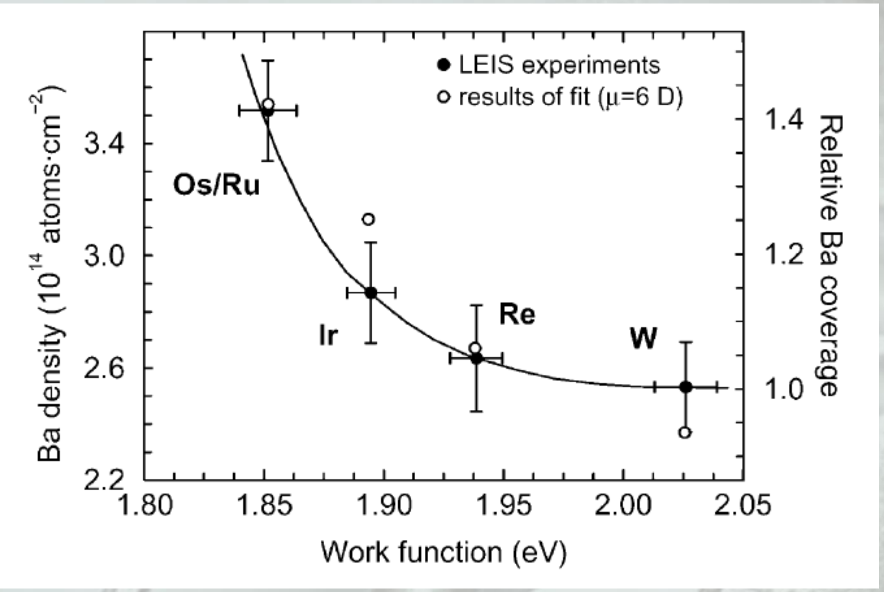


a) SAM mapping of Sc b) SAM mapping of Ba c) SAM mapping of O
of a LAD top-layer Ba-Scandate cathode of Philips operated in an electron gun after life. The length of the bar is 100 µm. One can see the central sputter “crater“ at the e-beam origin. In the center, Sc has been completely removed and only I cathode emission remains. It can be seen, that Ba needs an O bridge to better stick to the surface. This was also confirmed by R. Cortenraad et al. by LEIS investigations.

d) Low-energy Auger spectrum of Os/Ru-I cathode.
The peak marked Ba-O is a measure for Ba-O bonding and the peak marked Ba is a measure for Ba-density (see R. Cortenraad et al., Appl. Surf. Sci. 191 (2002) [8]).

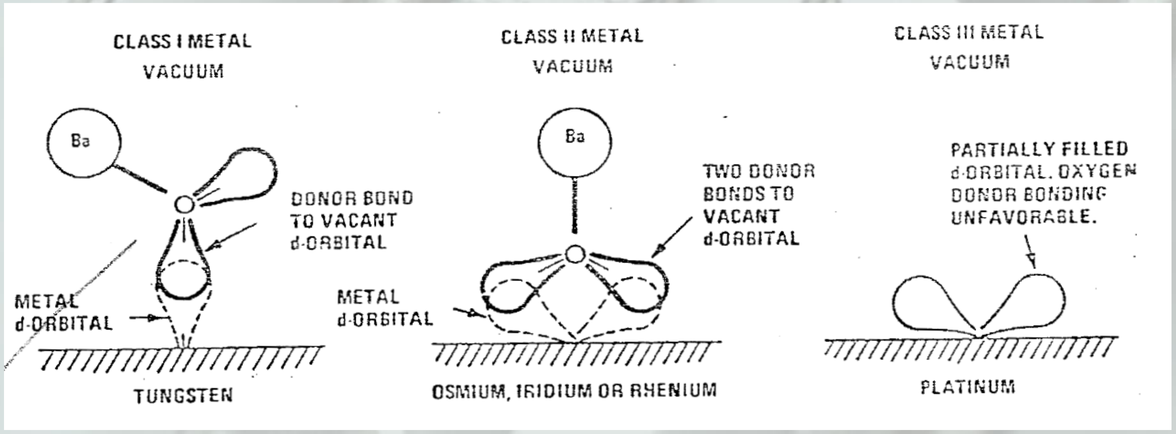


3.2 Surface analysis results and model for Ba dispenser cathodes



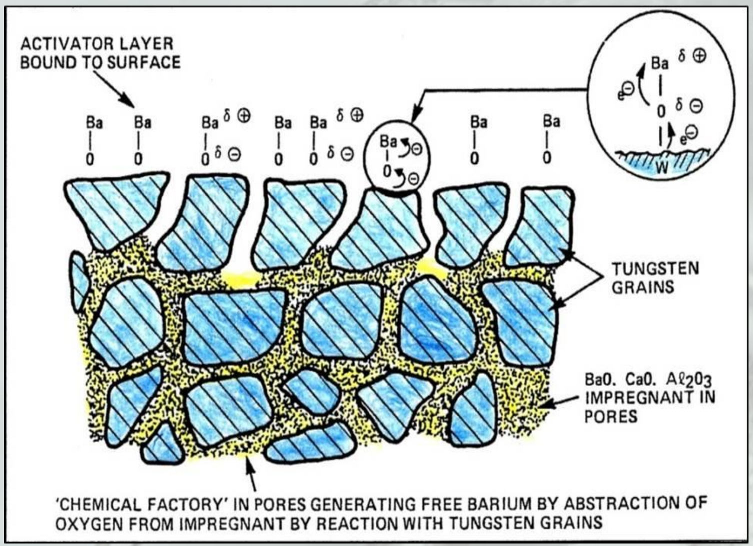
Ba densities as derived by LEIS for the different I cathode types (filled circles) versus WF. The right scale gives the relative Ba coverage w.r.t. tungsten [8]

W atoms have a single vacant d-orbital protruding normal to the surface, which bonds with a filled O orbital. Re, Ir, and Os atoms have two vacant d-orbital lobes available and are oriented suitably for bonding with two O orbitals according to M. Green (see [2], chapter 2). Hence a Ba-O coverage of the cathode higher than half a dipole mono-layer as for a W base can be achieved.



Covalent bonding to metal surface d orbitals: From M. Green „Dispenser Cathode Physics“, Report RADC-TR-81-211, (1981) and G. Kornfeld, NTG 95, 1986

3.3 Ba supply mechanisms of Ba dispenser cathodes



Ba is generated via a wall reaction between the impregnant in the pores and the tungsten pore walls at elevated temperatures. There exist different compositions of the impregnants, typically Ba.Ca.aluminates. Mostly used are „411“ or „532“, which means $4BaO.CaO.Al_2O_3$ or or „532“ for $5BaO.3CaO.2Al_2O_3$

E. Rittner 1957 (see Lipeless, [9]) proposed the following Ba generation reaction for 532:

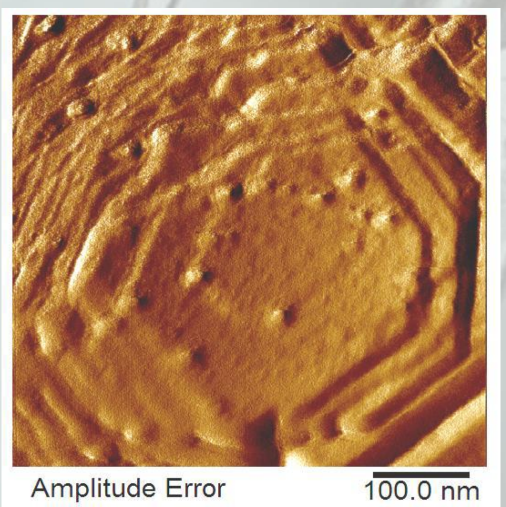
$5BaO.3CaO.2Al_2O_3 + \frac{3}{4} W \rightarrow \frac{3}{4} Ca_2BaWO_6 + \frac{3}{4} Ca_2BaAl_2O_6 + 5/4\ BaAl_2O_4 + 9/4\ Ba$ (1)

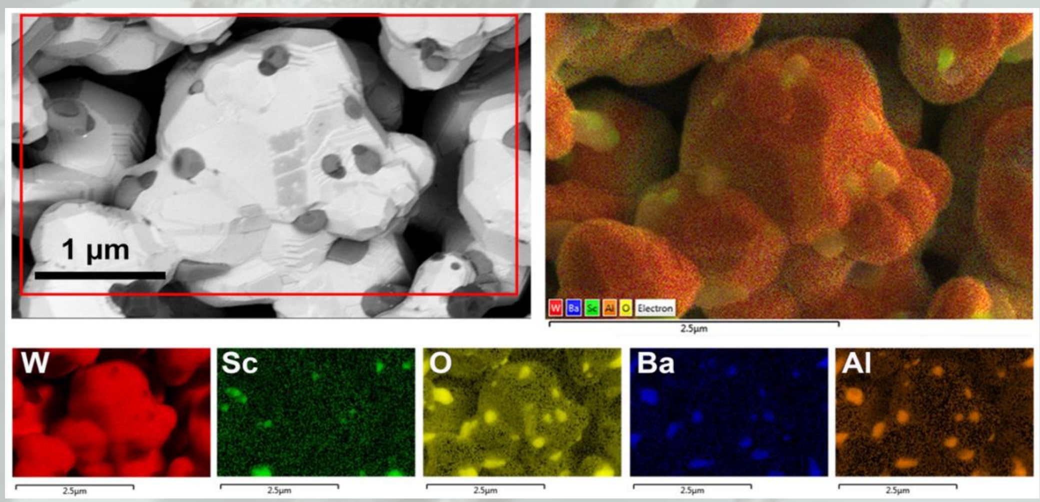
For 411 the sum reaction was not established, but A. Shroff found the main reaction products BaAlO4, BaWO4 and CaWO4 [10], which is in line with the following sum reaction (GG):

$4BaO.CaO.Al_2O_3 + 2\ W + 2\ O_2 \rightarrow BaWO_4 + BaAlO_4 + CaWO_4 + 2\ Ba$ (2)

4.1 Surface analysis results for Ba scandate dispenser cathodes

a) SEM micrograph (above) **b) Ba SAM mapping** **c) SAM : Re (green) & Sc (yellow)**
of **LAD top layer Scandate cathode** in the central beam emitting region **after ion bombardment**; the cathode was re-activated for 30 min at 1060°C $_{\text{Mo-Br.}}$ and then kept at 965°C $_{\text{Mo-Br.}}$ during SAM [4].





SDD Cathode (Y. Wang et al., J. Balk, B. Vancil et al., [4]); SFM (left) , SEM (center) and SAM micrographs; separate Sc containing nanoparticles!

4.2 Emission model of Ba scandate dispenser cathodes

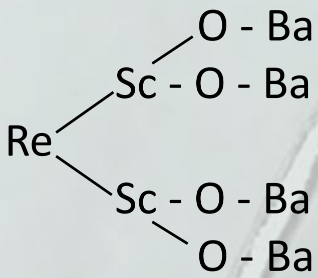
There is the paradox situation, that Scandate cathode show unprecedented **high emission** capability, but evidently only **from small spots of a Ba, Sc and O compound,** which means low coverage (consistant with low Richardson constants).
A **work function $e\Phi_R$ = 1.15 eV ± 0.05 eV** was obtained for all types of scandate cathodes also during deterioration, namely the WF of the highly emitting patches.
The **high emission** was quantitatively **explained** by G. Gärtner via the **beamlet effect first introduced by Hasker**, where microbeams show a much higher emission current density than the space charge limited density [2-4].
This results in a **superposition model** of highly emitting **scandate cathode** (semiconductor) **patches**, surrounded by **W - I or Re - I cathode emission**.

S. Yin et al. at IVEW/ IVESC 2020 proposed a **binary tree model** of the form

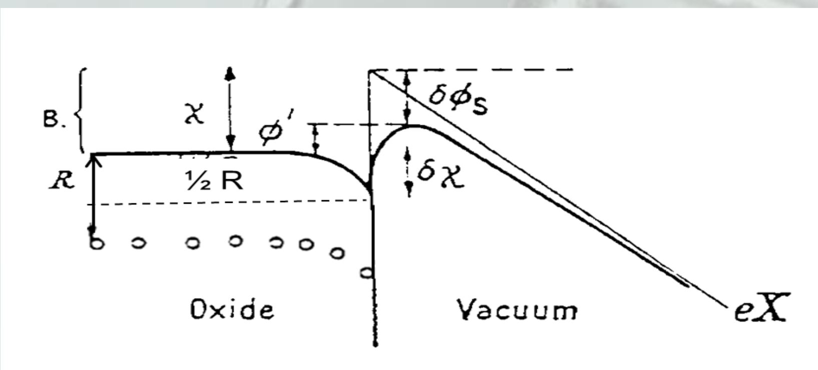
.   O-Ba
W - O- Sc   with a higher density of Ba at the surface [6]
             O-Ba

The model of S. Yin was not really worked out in detail as that by M. Green for Ba dispenser cathodes using covalent bonding theory. S. Yin also introduced an error : W base of M cathode instead of Re, Ir or Os!! It should be reformulated by regarding the outer bonding orbitals of Sc ([Ar] $3d^1$ $4s^2$) and their respective energies.
Cluster model calculations have been carried out by **W. Müller** and a **model system** was investigated by **P. Zagwijn** et al. with **WF 1.18 eV**, both presented **at IVESC 1996**.

4.2f Emission model of Ba scandate dispenser cathodes



If one modifies the Green model for M cathodes, as an alternative also **two Ba-O dipoles** could possibly **attach on Re**! In combination with Yins model, then 2 binary trees could attach. This could further increase the Ba-O dipole layer coverage and reduce the WF (**multi-layer model**)



Schematic energy levels in an oxide coating according to Wright and Woods, but corrected for the Fermi level, when space-charge and Schottky effects; WF is modified to $\Phi' = \Phi - \delta\chi - \delta\Phi_S$; the open circles are the donors.

S. Yin [6] extended his „model“ to a larger cluster with 8 Sc atoms and 16 Ba atoms, which in the end leads to larger atomic Sc_2O_3 semiconductor clusters and finally will end up in a **semiconductor model**, pioneered for Sc-I by **Maloney** and described in [2], chapter 4. In both the dipole model and in the semi-conductor theory the **outer layer of Ba ions** reduces the work function, in the latter by **band bending superimposed on the mirror image charge in an exernal field**.

It is very instructive to study the SAM mappings for Sc, O, Ba in more detail; in case of LAD scandate cathodes it was observed, that the Ba and O structures were somewhat larger than the thicker Sc structures: in conclusion Sc-oxide seems to act as an O source, leading to a **O – Ba dipole layer halo** (binary tree halo?): see appendix

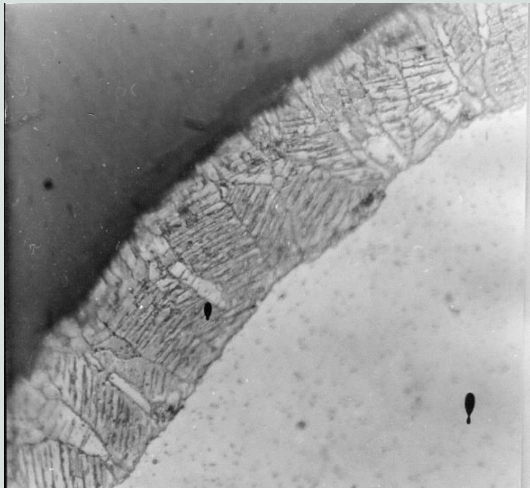
5. Surface analysis results for Th dispenser cathodes and Th supply mechanisms

By generation of electropositive **monolayer of Th on W**, the **WF eΦ = 2.7 eV** is by far lower than the WF of tungsten of 4.54 eV and even lower than the WF of Th of 3.5 eV.
The supply of Th is achieved by embedding ThO_2 particles in the tungsten grains and by carburization of the top-layer, e.g. of 1/10 to 1/3 of the wire radius, usually by heating the wire in an gas atmosphere with a hydrocarbon compound.
Free atomic Th is generated via the reaction:

$$2\,W_2C + ThO_2 \rightarrow 4W + CO\uparrow + Th \qquad (3)$$

Th migrates to the surface via grain boundary diffusion and spreads over the surface via surface diffusion [1,11].

The density of the Th mono-layer was determined by W. Danforth et al. in 1960 [13] via successive accumulation on a micro-balance to 4,2 $*10^{14}$ atoms /cm^2
Of course the existence of a Th monolayer can also be proven by modern methods e.g. by AES or LEIS. AES investigations by K. Ishikawa et al. in 1976 (Japan. J.A.P 15, 1571f [14]) gave the result, that Th is directly bound to W (no O-bridge).
H. Kim and K. Okuno in 1979 found, that by coadsorption of hydrogen (1 ML) on Th-W, the work function could be further reduced by 0.23 eV.



Surface structures of thoriated tungsten and influence on Th coverage and Richardson constant A_R:

a) Carburized thoriated tungsten wires:

The figure shows a cros section of a Th/W wire (D = 1mm) carburized in acetylene at T about 2050 °C to a depth of 82 µm ; typical is a low $\mathbf{A_R}$ of around **3 -4 A/(cm²K²)**;
Foto: van de Kroonenberg, Philips 1957

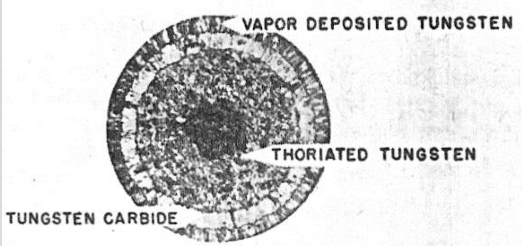
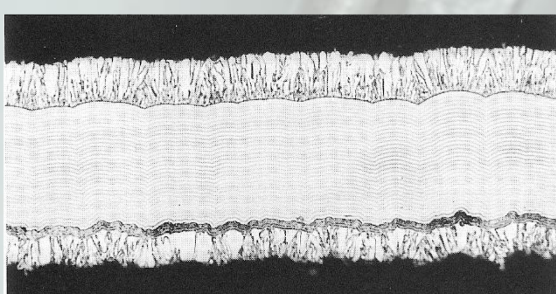


FIG. 1. Cross section of thoriated tungsten emitter with grain-oriented overlayer.

b) Carburized thoriated tungsten wires with preferentially oriented CVD W coating (100):

Investigations of I. Weissman of Varian in 1965:
He obtained **2.85 eV and $\mathbf{A_R}$ = 17 A/(cm²K²)** for the **CVD coated emitter** and **2.85 eV and $\mathbf{A_R}$ = 4 A/(cm²K²)** for the ordinary one, which implies an improvement in j by a factor 3, but measurements did not surpass j = 0.6 A/cm².



c) Cross section of free standing **thoriated tungsten cylinders prepared by PCVD** by G. Gärtner et al. from Philips in the years 1983 – 1985; the wall thickness is about 70 µm. The starting compounds for PCVD were WF_6, H_2 and a Th-β-diketonate. For emission tests discs of 2 mm diameter were cut from the walls , mounted on a heater and were also carburized. They showed twice the saturated emission j compared to standard wires. The best result was WF= **2.85 eV and $\mathbf{A_R}$ = 22.8 A/(cm²K²)**

6. Other types of dispenser cathodes:

a) La-Mo dispenser cathodes

By replacing Th by La and W by Mo, the lanthanated Mo cathode was pioneered by C. Buxbaum et al. of BBC in the years 1976 – 1983 [15], also for use in RF tubes. Mo is also carburized similar to W and the following sum reaction for La resupply is obtained (without Pt):

$$2\ Mo_2C + 2/3\ La_2O_3 \rightarrow 4\ Mo + 2\ CO\uparrow + 4/3\ La \qquad (4)$$

A further improvement was a thin surface coating with Pt, which provides a higher sticking coefficient for La. The cathodes can deliver 3.5 to 8 A/cm^2 in the temperature range 1500 to 1630 °C.

b) Metal-alloy dispenser cathodes:

These cathodes have been investigated by B. Djubua et al. in Russia in the years 1966 – 2003 [16] and they have been applied in RF- and microwave tubes: Especially Ir_2La (Ir_5La) with a WF of 2.2 eV and Ir_5Ce with 2.6 eV. The monoatomic layer is either La or Ce. The cathodes are robust versus ion bombardment and poisoning. Ir_2La can deliver 10A/cm^2 pulsed at 1514 °C for 10000 h. The metal-alloy cathodes also have a high secondary electron emission coefficient.

7. Discussion and Conclusions:

In the case of **Ba dispenser cathodes** a **Ba monolayer** is provided on the cathodes surface **via an oxygen bond** to the d-orbitals of the base metal. The Ba-O dipole results in a work function even lower than the WF of Ba. The higher emission of Os/Ru-I, Ir-I and Re-I compared to W-I is explained by the higher Ba density caused by two instead of one d orbital.

For **Ba scandate dispenser cathodes also a Ba monolayer** is supplied, which spreads over I cathode fractions (W-I, Re-) and over scandia containing emissive dots. There it is **either an oxide cathode type emission** with an oxygen deficit at the surface, **or a bond to Sc with two oxygen bonds to Ba (multi-layer)**. It has to be noted, that **in a wider sense also Ba-oxide cathodes are dispenser cathodes**, since the Ba monolayer is provided by an exchange reaction of the activators (Mg, Al, W etc.) with BaO.

In the case of **Th/W and La/Mo** also **monolayers of Th or La spread over the surface**, but are **not bonded via** an **oxygen** bridge. Here an additional hydrogen bridge would provide an advantage. For the metal-alloy cathodes also a monolayer of the low work function atoms is claimed, but unfortunately no high resolution surface analysis results have been reported.

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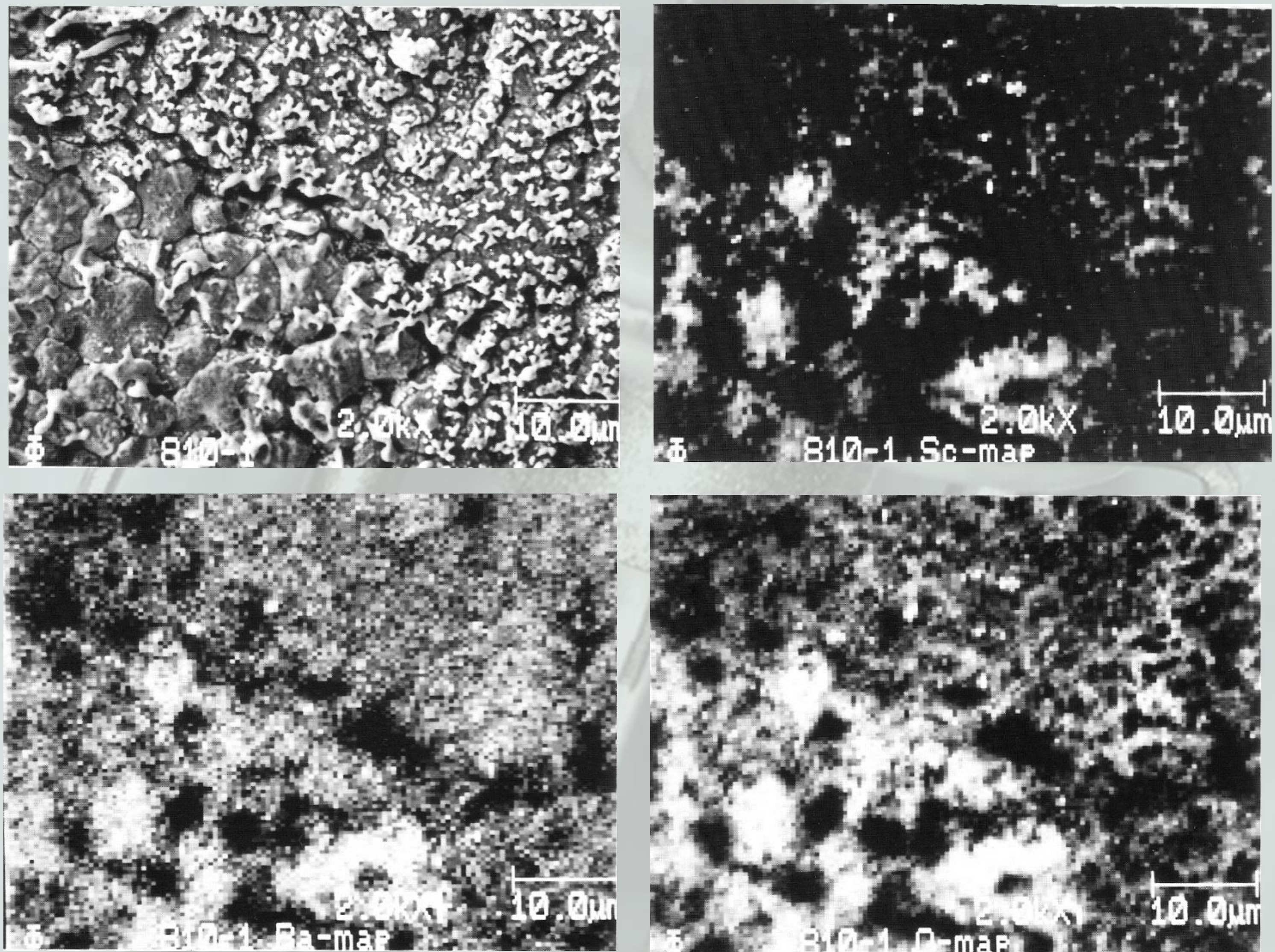
Thank you for your attention

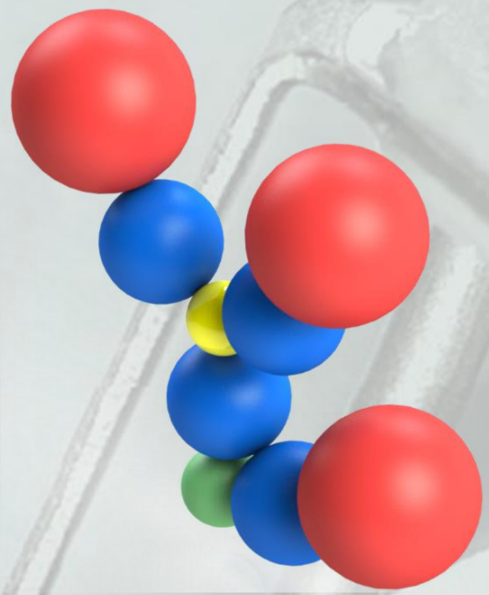
Vielen Dank für Ihre Aufmerksamkeit



LAD Scandate cathode: top left: SEM micrograph; top-right: Sc SAM mapping
Bottom left: Ba SAM mapping; bottom right: O SAM mapping: Ba and O structure extensions are a bit larger than Sc structures !!

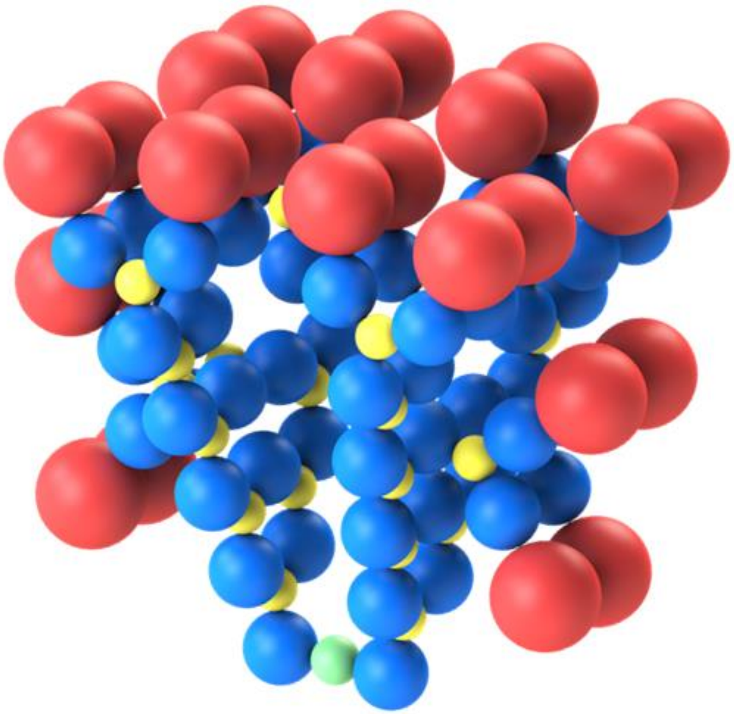
Remark:
In case of Th/W which was intensely studied in the 1930s to 1950s,
the temperature dependent Th diffusion length turned out to be much lower than predicted from grain boundary and surface diffusion and evaporation, which was explained by Langmuir by an edge effect of higher Th evaporation at the boundary edges;
This could also be enhanced by the parallel CO ejection.
The low Richardson constants for thoriated tungsten wires could alo be explained by the decreasing Th surface coverage with temperature!

For Ba scandate cathodes the author has observed an interesting halo-effect around the scandia spots, with a larger extension of higher Ba and O density around these spots



This is his original scetch of the binary tree model of the M cathode, but it wrong w.r.t. tungsten and in contradiction to Green. M means: Re, Ir or Os as base metal !
If one modifies the Green model for M cathodes, as an alternative also two Ba-O dipoles could possibly attach on Re, Ir or Os!
This would then be in accordance to this figure. It should work perfectly for Scandate cathodes with an Re base, but not for W!!
S. Yin did not take the Sc electron configuration [Ar] $3d^1$ $4s^2$ into account.
He then extended his „model“ to a larger cluster with 8 Sc atoms and 16 Ba atoms, but neglects, that he then could better have regarded an atomic Sc2O3 cluster with corresponding surface states, which then approaches a **semiconductor model**.
In the end, only in case of a Sc-O-Ba layer on the metal base it can be regarded as a „model“.

Binary Tree Model of Scandate cathode



Typical structure

- There are 16 Ba^{+} ions on the outmost layer, and 8 Sc^{3+} ions on the second outmost layer in height direction;
- Other 8 Ba^{+} ions and 4 Sc^{3+} ions are on the side branches;
- The total Ba:Sc molecular ratio is 24:12 or simpified 2 : 1, which is perfectly consistent with that of our salt recipe.

S. Yin, ITG/IVEW & IVESC 2020