北京工業大學
BEIJING UNIVERSITY OF TECHNOLOGY

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Preparation of dispenser cathodes by fast sintering method

Jinshu Wang

College of Materials Science and Engineering,
Beijing University of Technology

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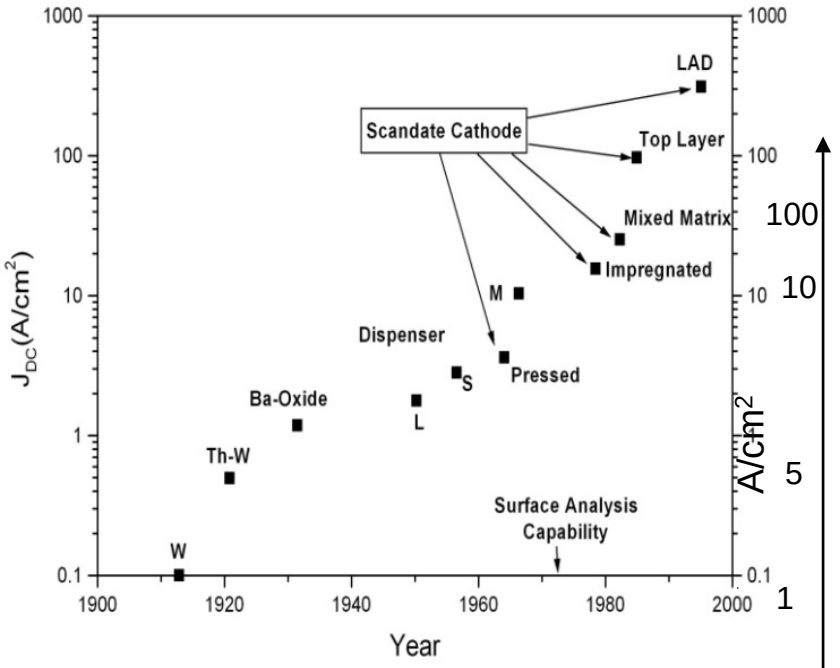
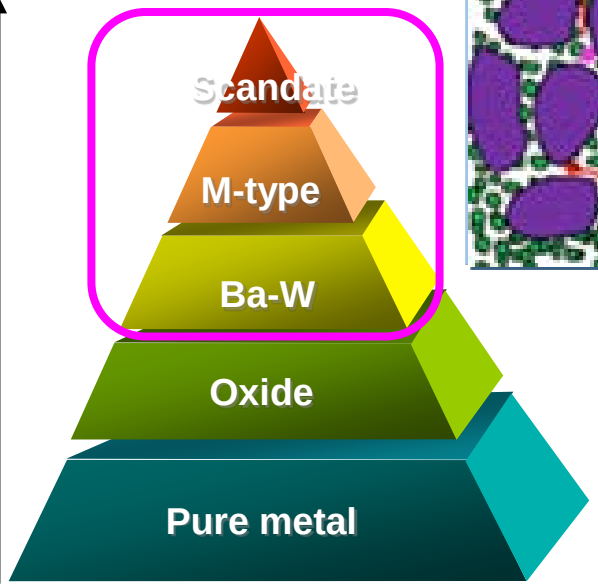
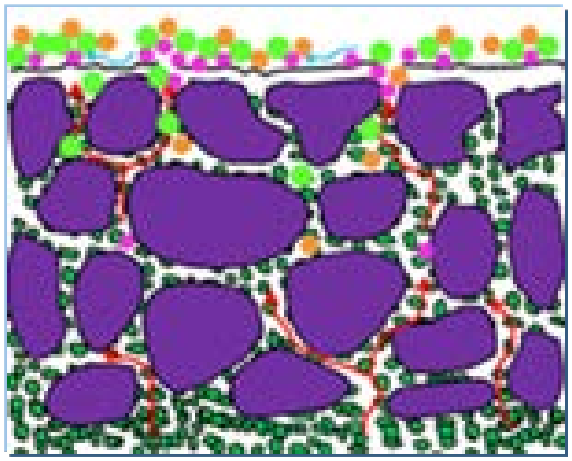
Outline

- 1. Background
- 2. Ba dispenser cathode prepared by selective laser melting technology
- 3. Scandate cathode prepared by microwave sintering method
- 4. Re_3W matrix cathode
- 5. Conclusions

Types of thermionic cathodes







Ba-W cathode have been extensively investigated but their emission current densities are insufficient.

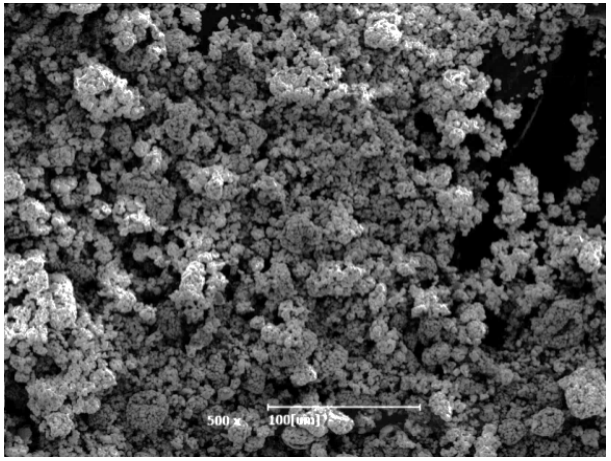
M-type coating cathode is the mostly used cathode.

Scandate cathode suffers from relatively low ion bombarding insensitivity.

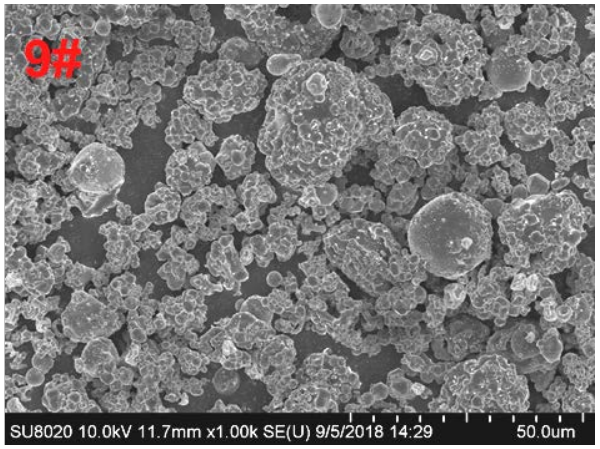
Ba dispenser cathode prepared by selective laser melting technology

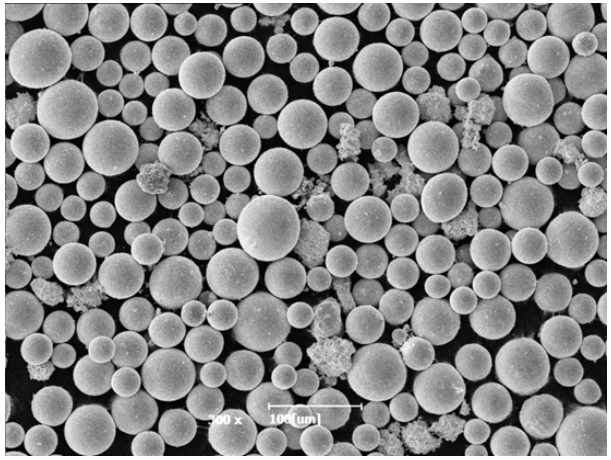
Powder preparation

Original W powder



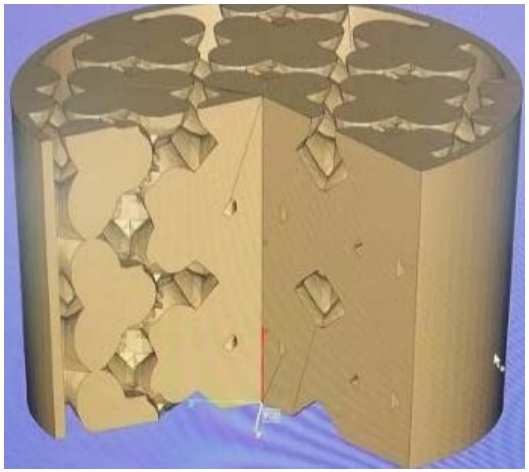
Granulated W powder by spray drying method



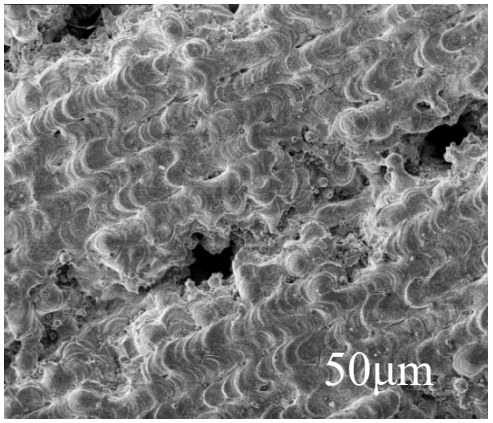


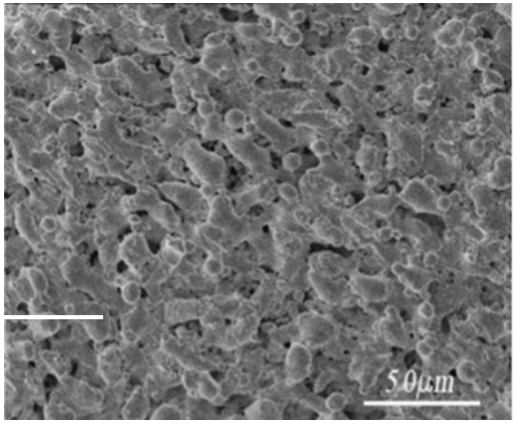
W powder after plasma spheroidization

Tungsten matrix design and preparation

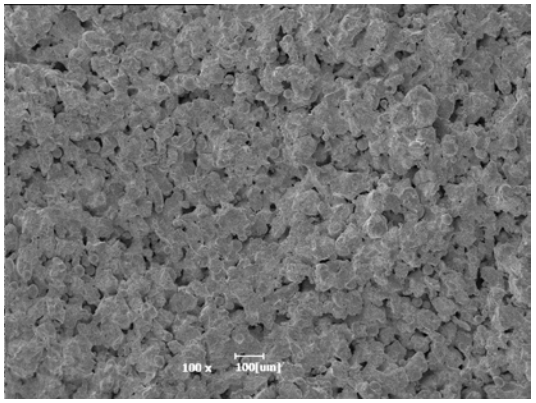


3D printing grid structure model with the porosity of 25% in the tungsten matrix





SEM images of tungsten matrix surface



SEM image of the cross-sectional morphology of the tungsten substrate

Scandia added 411 impregnations:

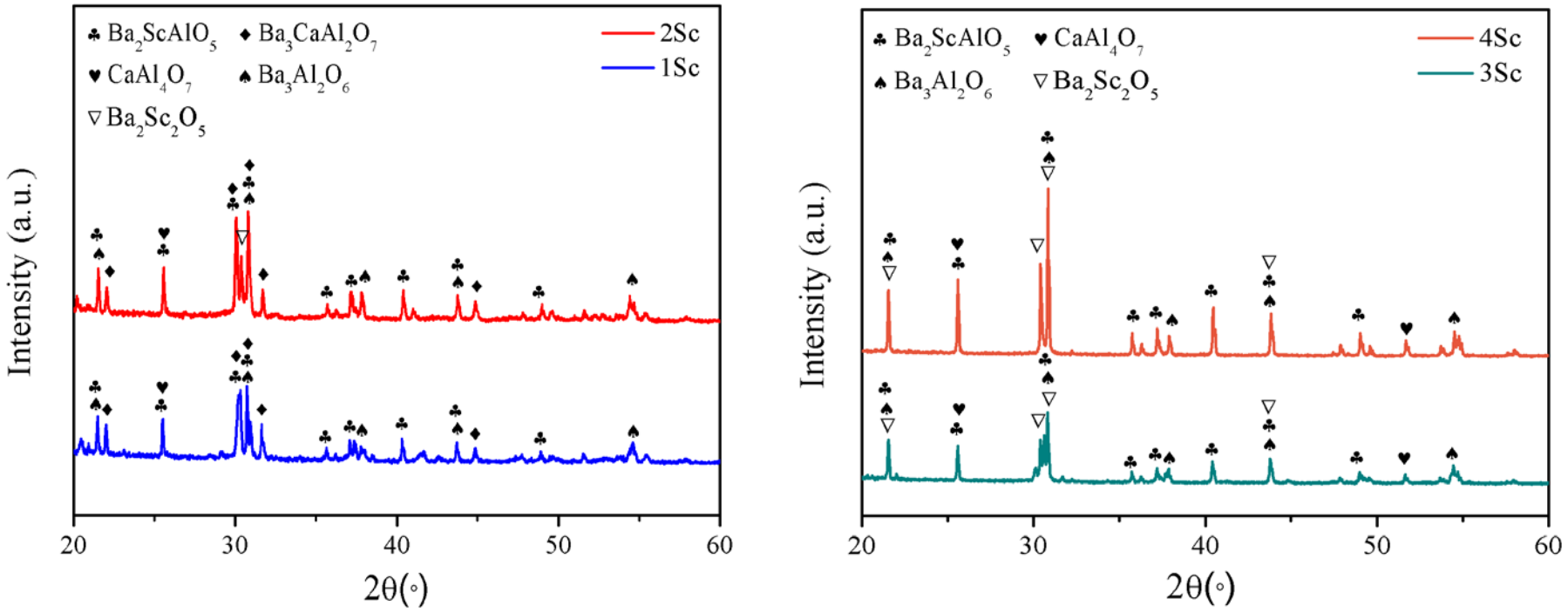


Fig. XRD spectrum of 411 Aluminates adding different Sc_2O_3 contents
a）411-1Sc，411-2Sc；b）411-3Sc，411-4Sc

Emission property:

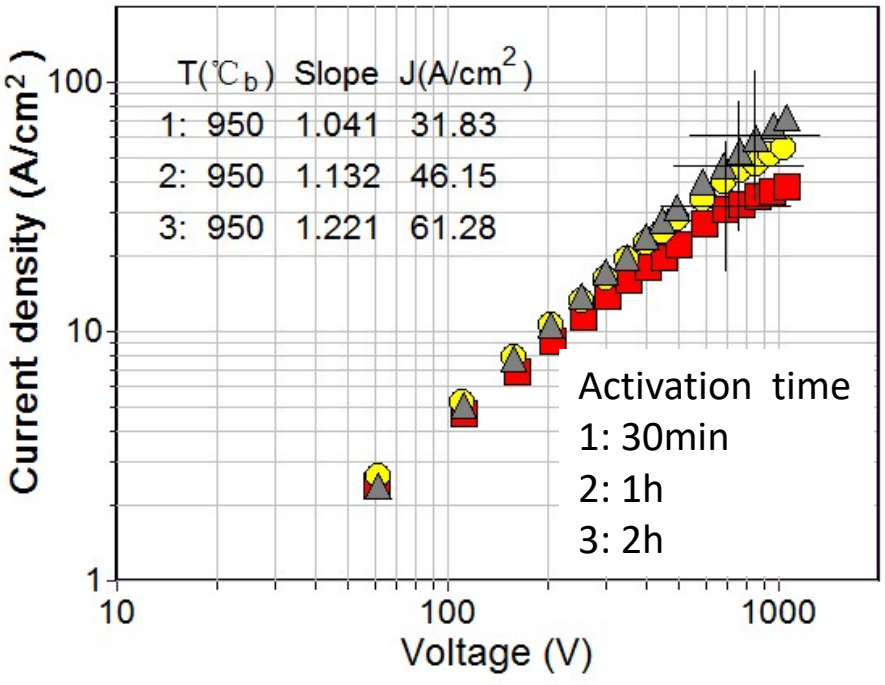


Fig. *LgI-LgU carves for Cathode at different activation time*

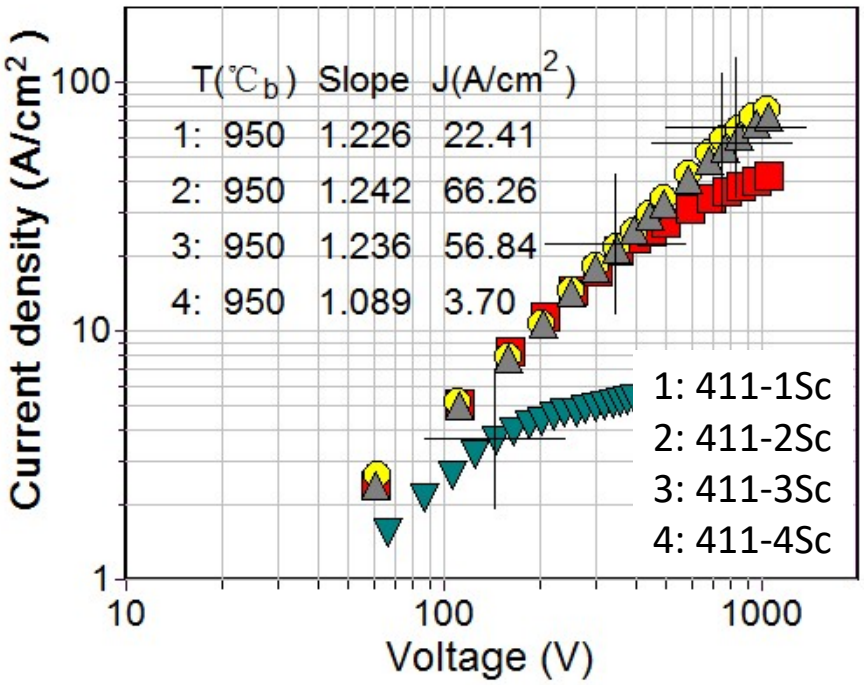


Fig. *LgI-LgU carves of the impregnated scandate SLM cathodes*

Scandate cathode prepared by microwave sintering method

Scandia doped tungsten powder:

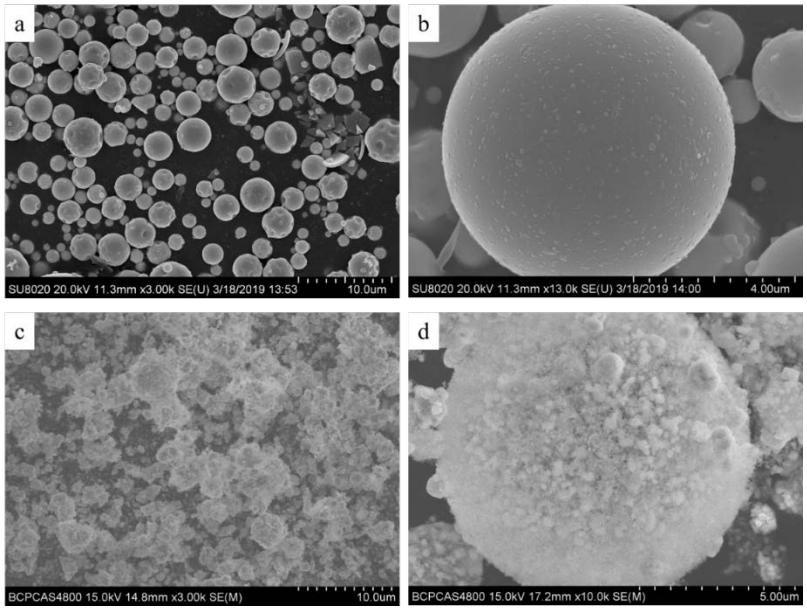
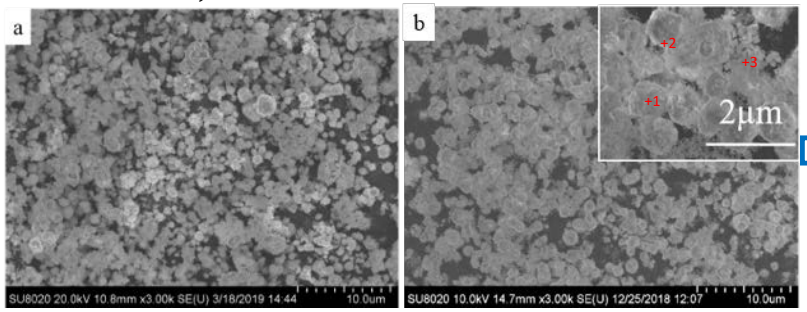


Fig. SEM images of the Sc doped W powder prepared by spray drying:
a.b: after calcination,c.d. after reduction



EDS

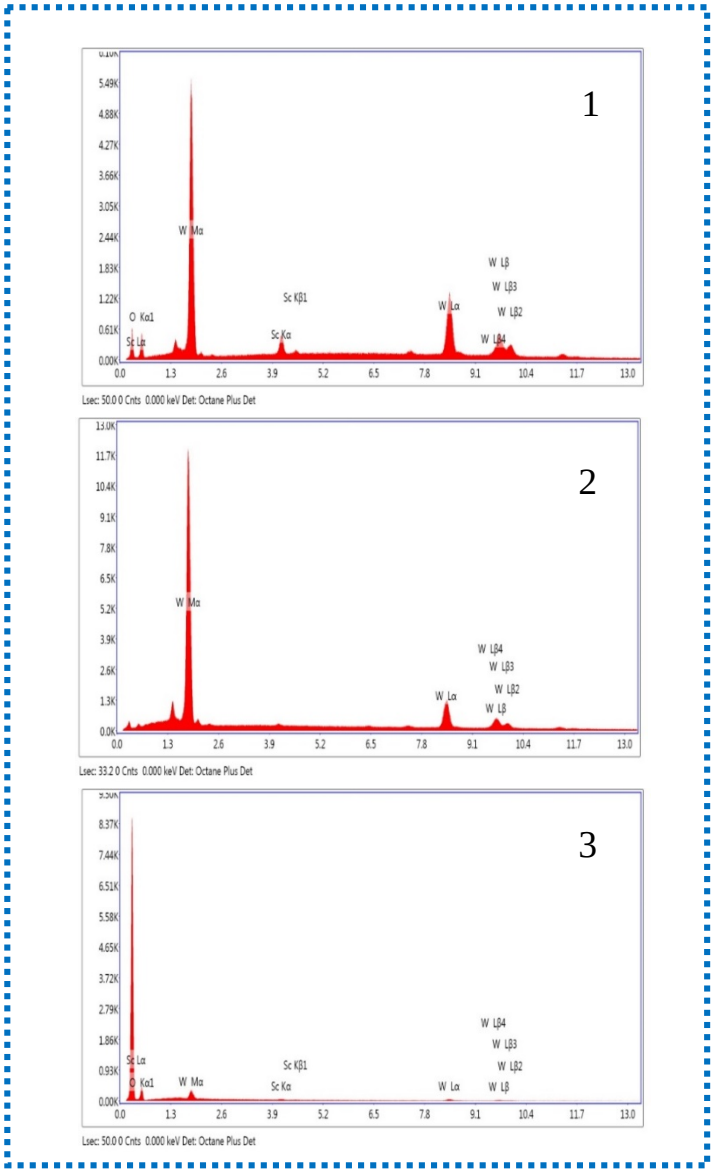


Fig. SEM images of Sc doped W powder prepared by sol-gel method
a. after calcination, b. after reduction, c. EDS spectrum analysis

Scandia doped tungsten powder:

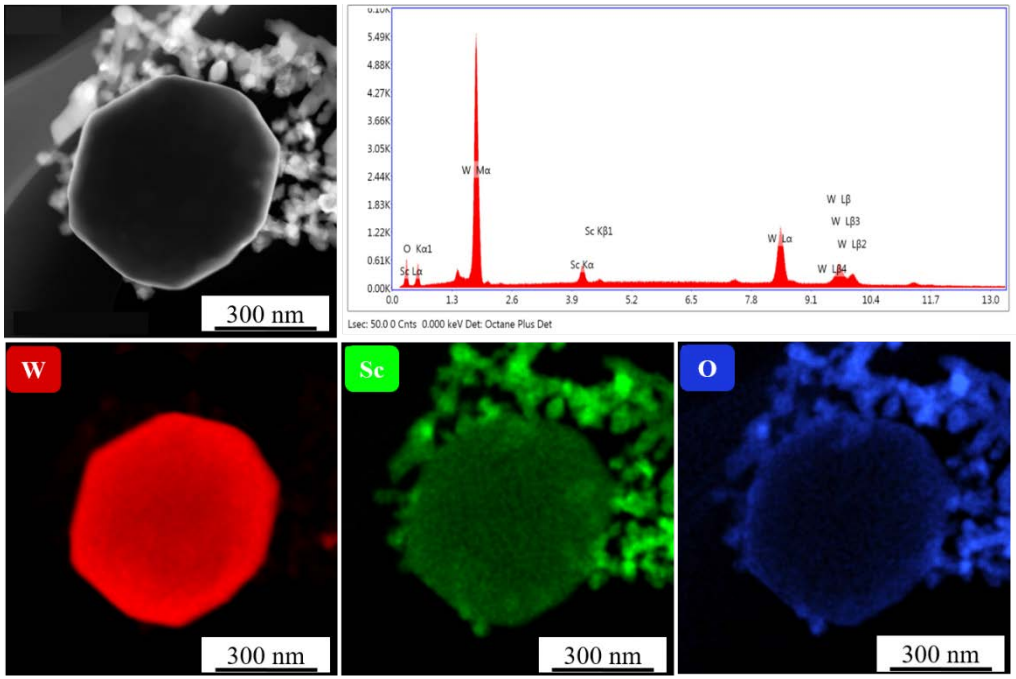


Fig.1 TEM of the Sc_2O_3 doped W powder after reduction

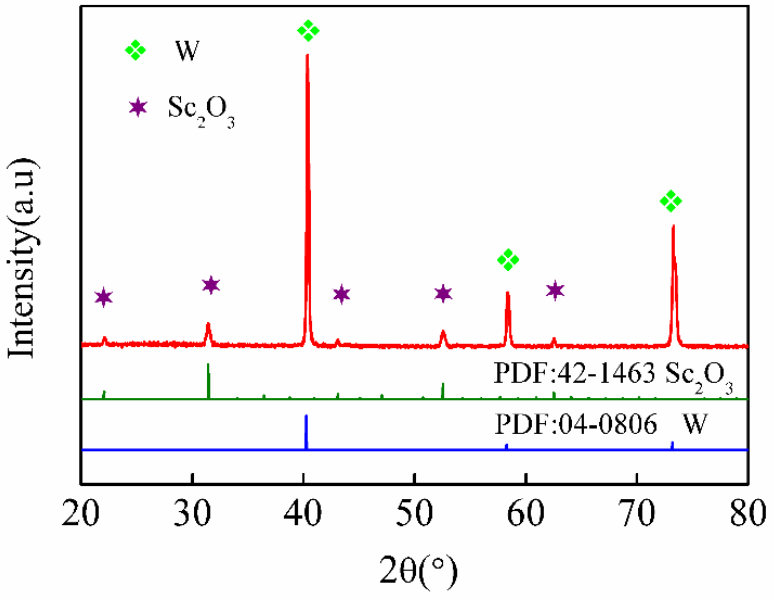


Fig.2 XRD of the Sc doped W powder after reduction

Nano sized Sc_2O_3 was covered on W

Sc_2O_3-W matrix:

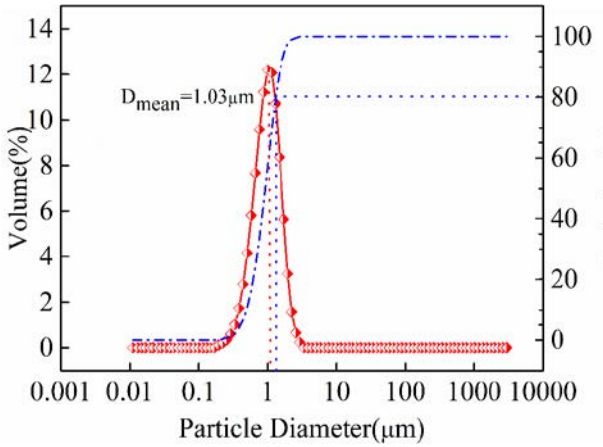


Fig.1 Particle size curve of Sc doped W powder after reduction

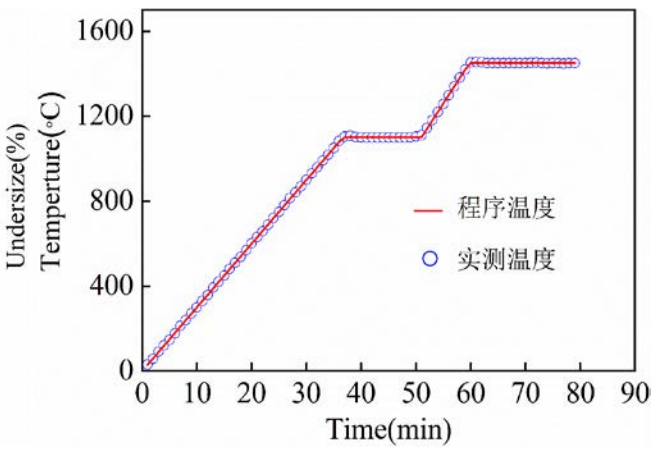


Fig.2 Microwave sintering trial sintering temperature rise curve

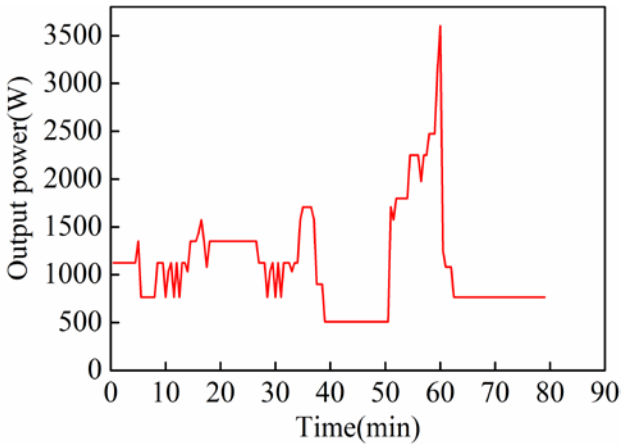


Fig.3 Microwave sintering trial sintering power curve

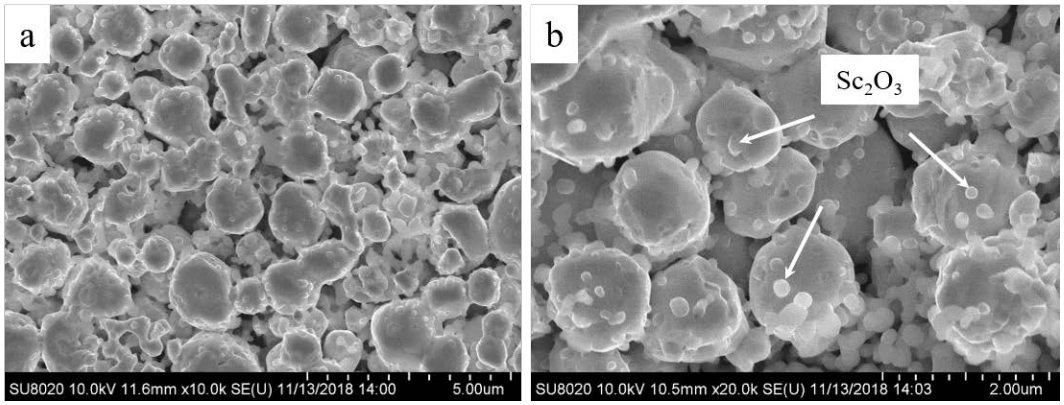


Fig.4 SEM image cathode surface ofcathode surface by 1300 ℃ microwave sintering

Sc_2O_3-W matrix cathode:

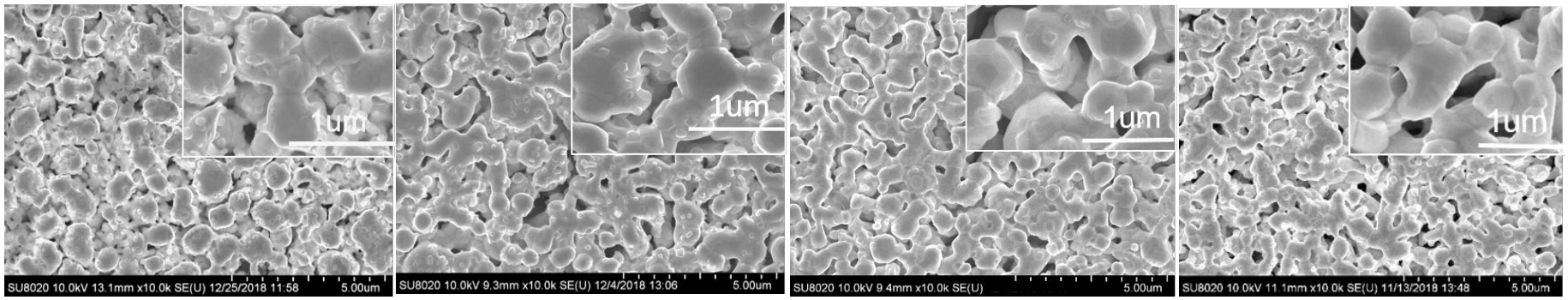


Fig.1 SEM images of the cathode matrix surface by different microwave sintering temperatures. 1375℃；1400℃；1425℃；1475℃

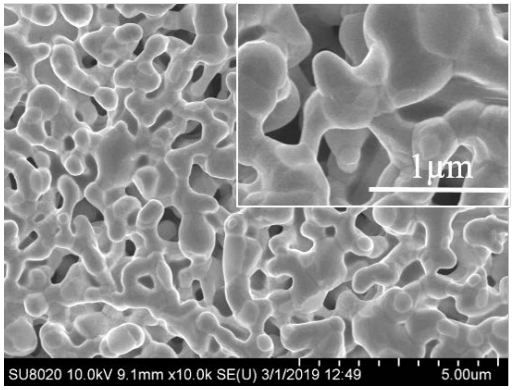


Fig.2 SEM images of the cathode matrix surface by 1450℃

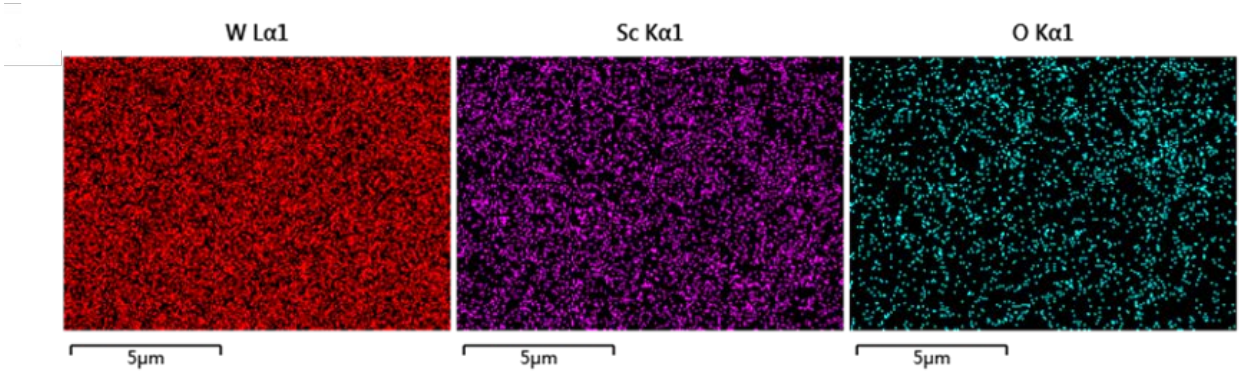
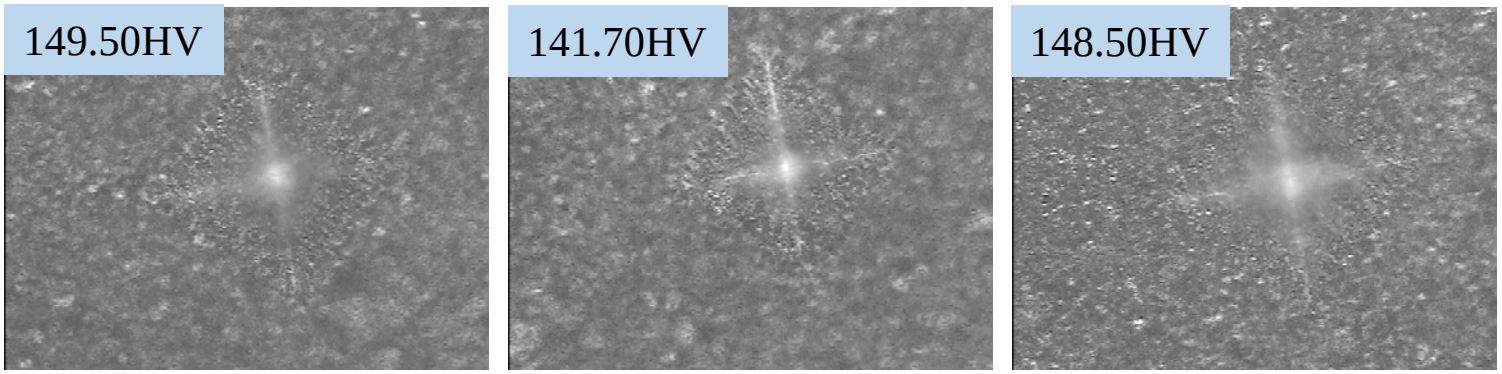


Fig.3 EDS surface scan results of 1450℃

Hardness of the Sc_2O_3-W matrix:



Load 200 g
Holding time 15 s

Fig.1 Three-point micro-hardness analysis of the cathode surface after conventional sintering

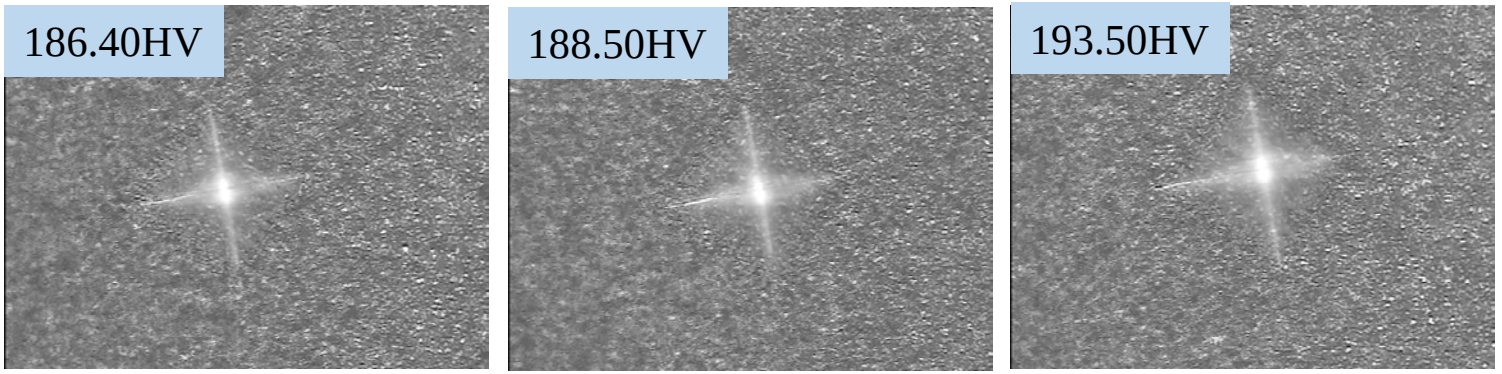


Fig.2 Three-point micro-hardness analysis of the cathode surface after microwave sintering

The matrix is relatively homogeneous

Emission property:

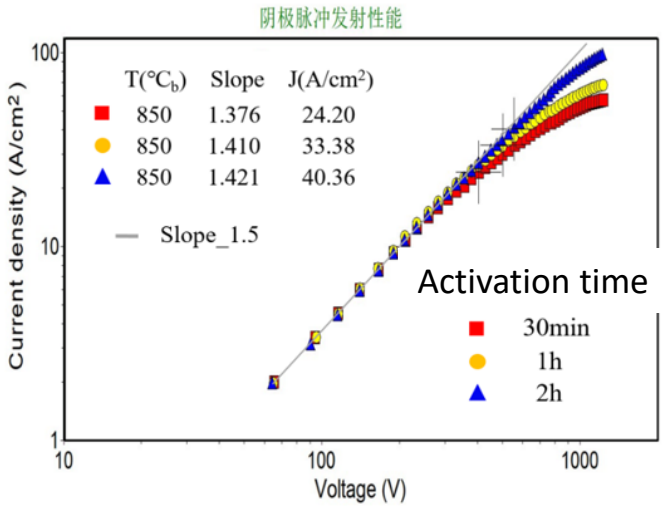


Fig.1 *LgI-LgU carves for Cathode at different activation time*

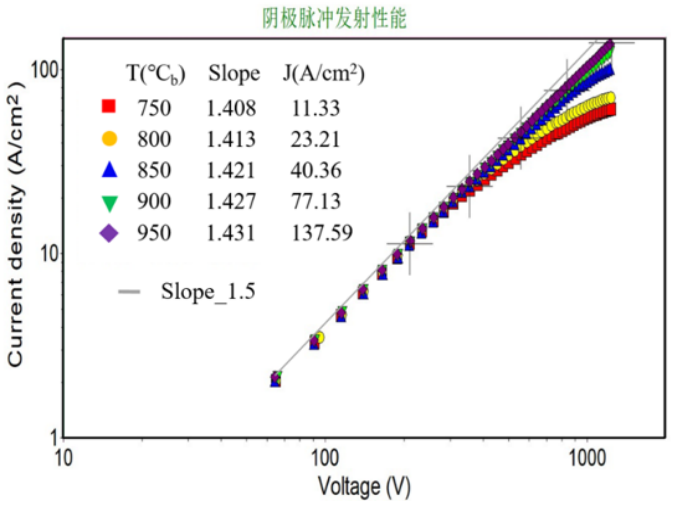


Fig.2 *LgI-LgU carves for Cathode at different temperature*

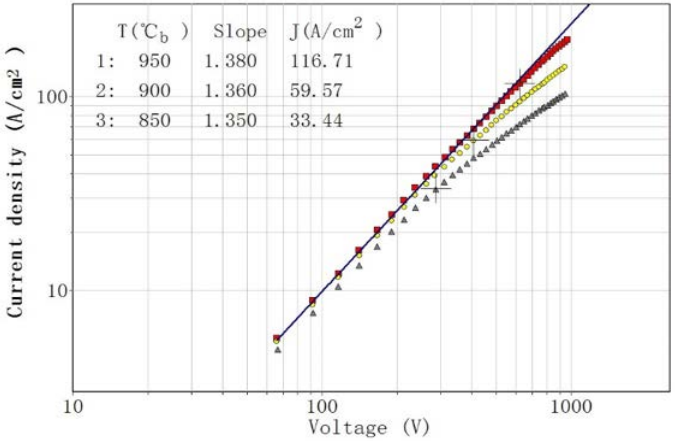


Fig.3 *LgI-LgU carves for PM Cathode*

The cathode has good emission uniformity

- Re-W matrix Ba dispenser cathode

Features of Ba-W cathodes

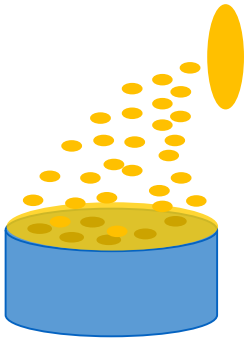
Deposition of noble metal thin films on Ba-W cathodes

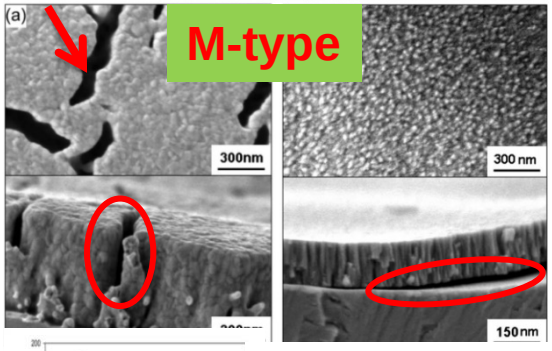
Advantages:

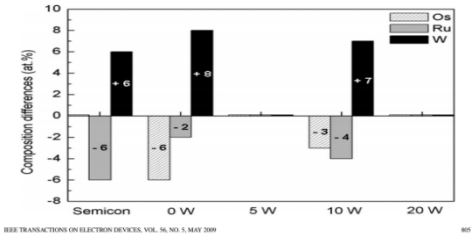
1. High emission ability（~10 A/cm^2）
2. Suitable for commercial production

Disadvantages:

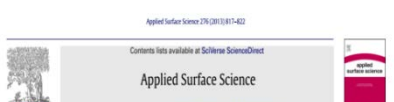
1. Poor interface adhesions
2. Block the holes for active substance diffusion
3. Film composition change with time

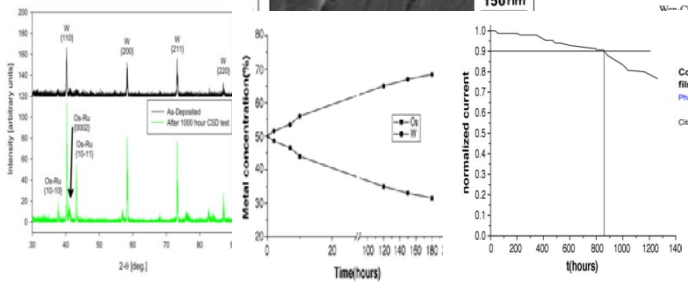


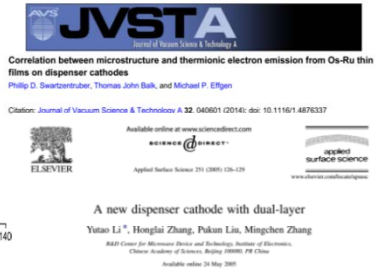


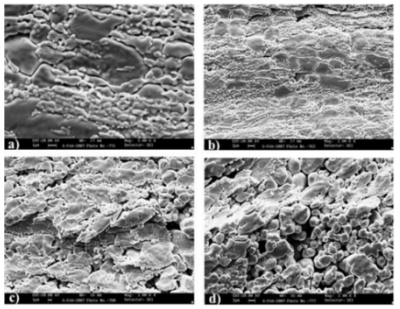


Effects of Substrate Bias on Microstructure of Osmium-Ruthenium Coatings for Porous Tungsten Dispenser Cathodes



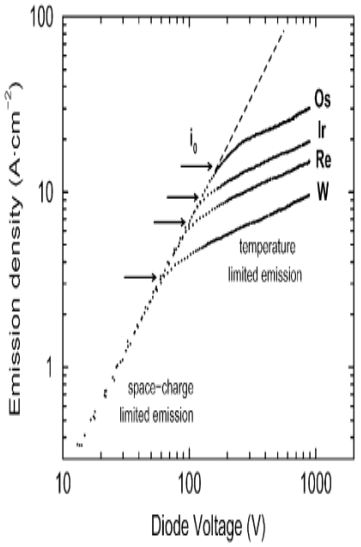






Advantages of Re addition

1. **Enhance ion bombarding insensitivity**
2. **Improve uniformity of electron emission**
3. **Refine the grains of substrate and improve the diffusion of active substance**
4. **Relatively cost-effective**



Surface analysis of thermionic dispenser cathodes☆

R. Cortenraad[a], A.W. Denier van der Gon[a,*], H.H. Brongersma[a], G. Gärtner[b], A. Manenschijn[c]

[a]Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands
[b]Philips Research Laboratories, Weisshausstrasse 2, D-52066 Aachen, Germany
[c]Philips Components, P.O. Box 218, 5600 MD Eindhoven, The Netherlands

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Emission property of scandia and Re doped tungsten matrix dispenser cathode

Jinshu Wang*, Yanchun Wang, Wei Liu, Lili Li, Yiman Wang, Meiling Zhou

School of Materials Science and Engineering, Beijing University of Technology, Beijing 100022, China

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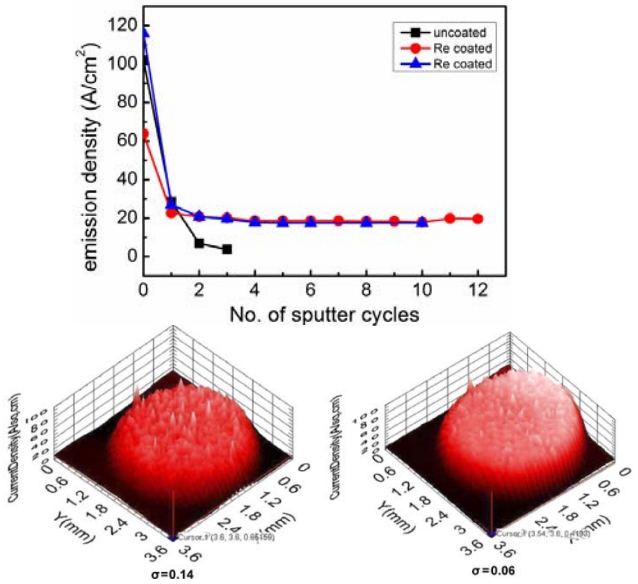
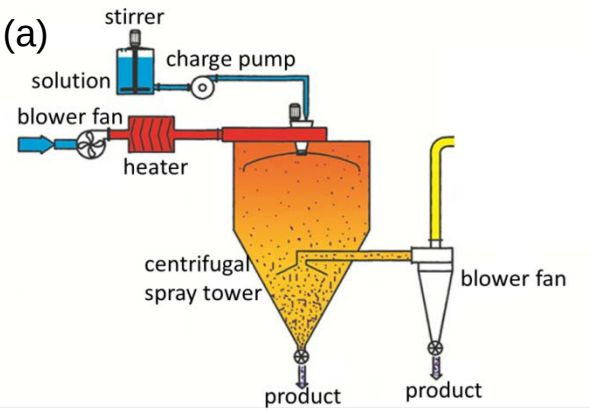


[1] R.Contenraad, et al. Appl. Surf. Sci. 191, (2002) 153-165.
[2] Udovan Slooten, et al. Appl. Surf. Sci. 111, (1997) 24-29.
[3] Jinshu Wang, et al. J. Alloys Compd. 459(1–2) , (2007) 302-306.

Reduction process of W-Re powders

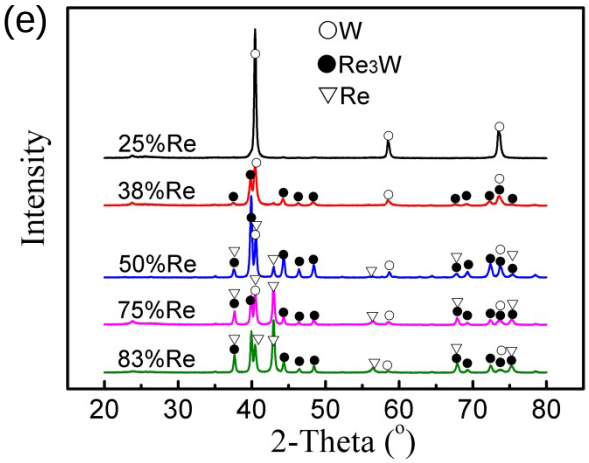
(a)



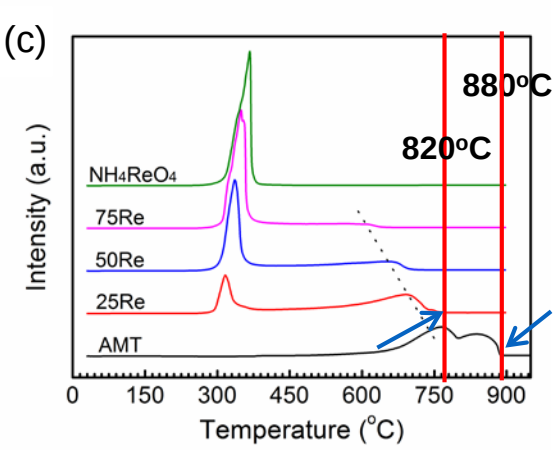
Powder Preparation Equipment

成分/编号	W(at%)	Re(at%)
W	100	--
25Re	75	25
38Re	62	38
50Re	50	50
75Re	25	75
83Re	17	83

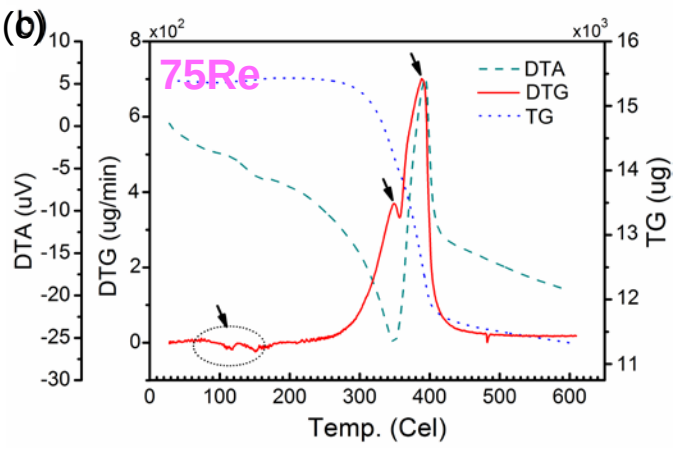
(e)



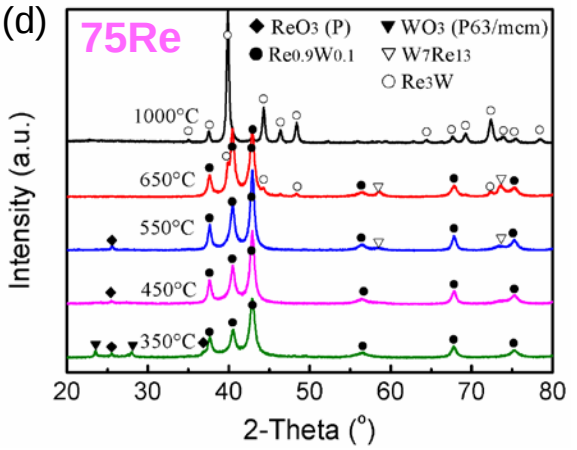
(c)



(b)



(d)



Reduction mechanism of W-Re powders

$$E_{ads(H_2)} = E_{H_2+slab} - \left(E_{H_2} + E_{slab}\right)$$

$$E_{des(H_2O)} = E_{H_2+slab} - \left(E_{H_2O} + E_{slab-O}\right)$$

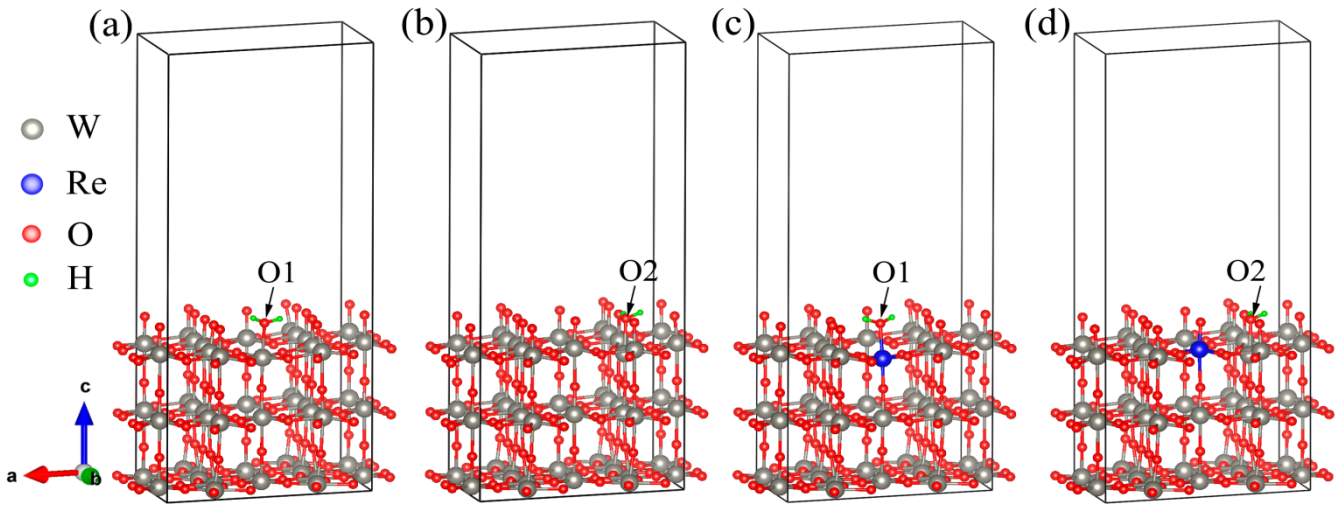
$$k = A\exp\left(-\frac{E_a}{k_B T}\right)$$

$$\frac{E_{a1}}{T_1} = \frac{E_{a2}}{T_2}$$

Configuration Energy (eV)	WO_3(001)		Re-doping WO_3(001)	
	O1	O2	O1	O2
Adsorption of H_2	-4.641	-4.631	-4.324	-4.882
Desorption of H_2O	1.177	1.163	1.124	1.142

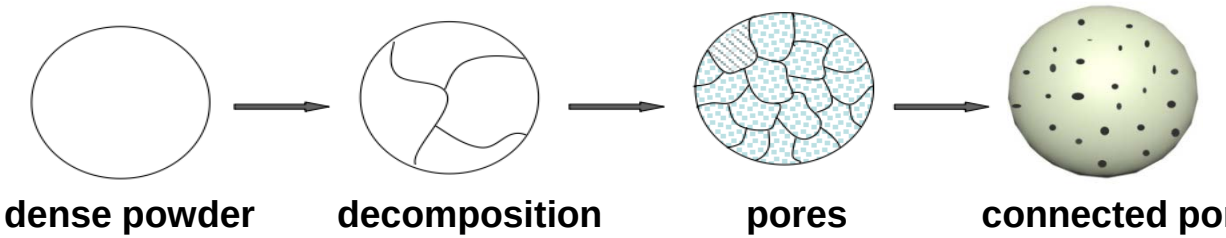
T1~880°C=1153K

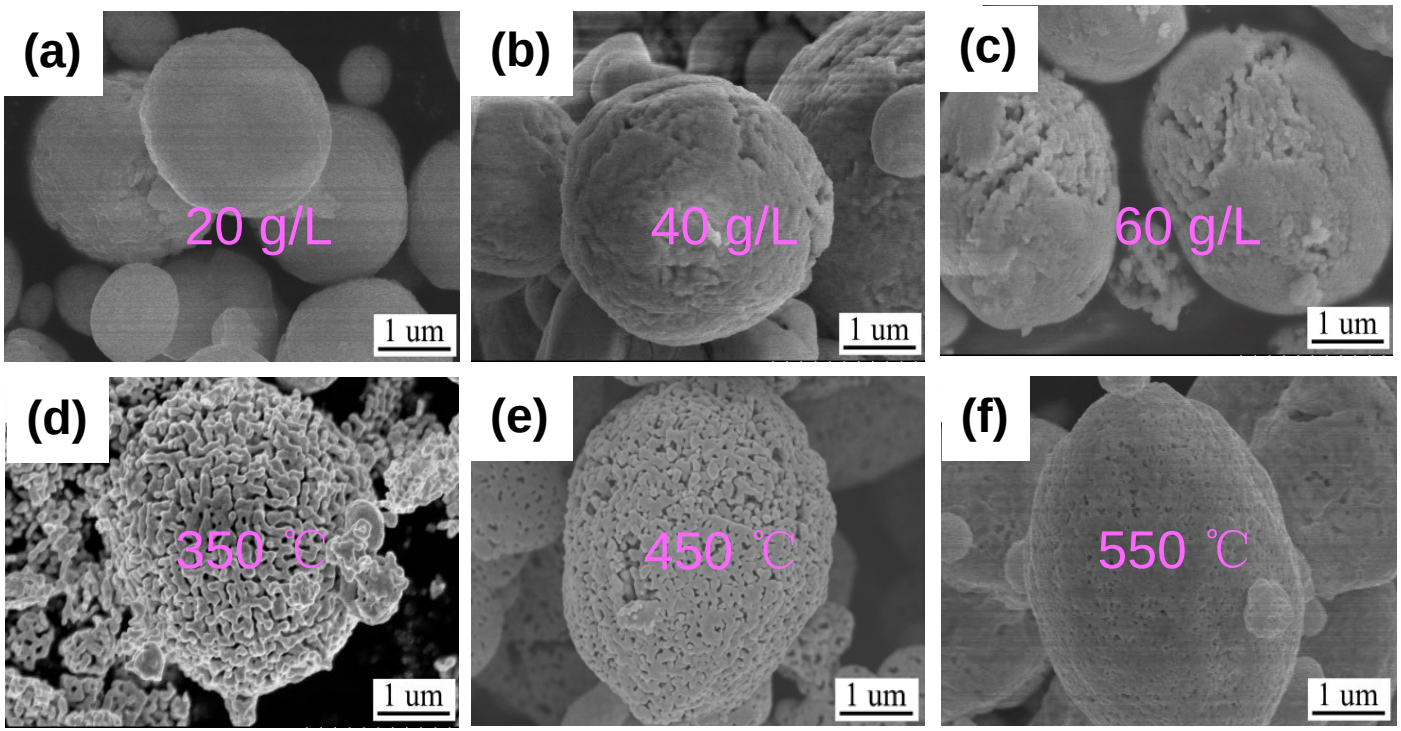
T2~1098K=825°C~820°C



Chen Lai, Jinshu Wang . Reduction, sintering and mechanical properties of rhenium-tungsten compounds, J. Alloy. Compd. 735, (2018) 2685-2693.

Powder morphology control

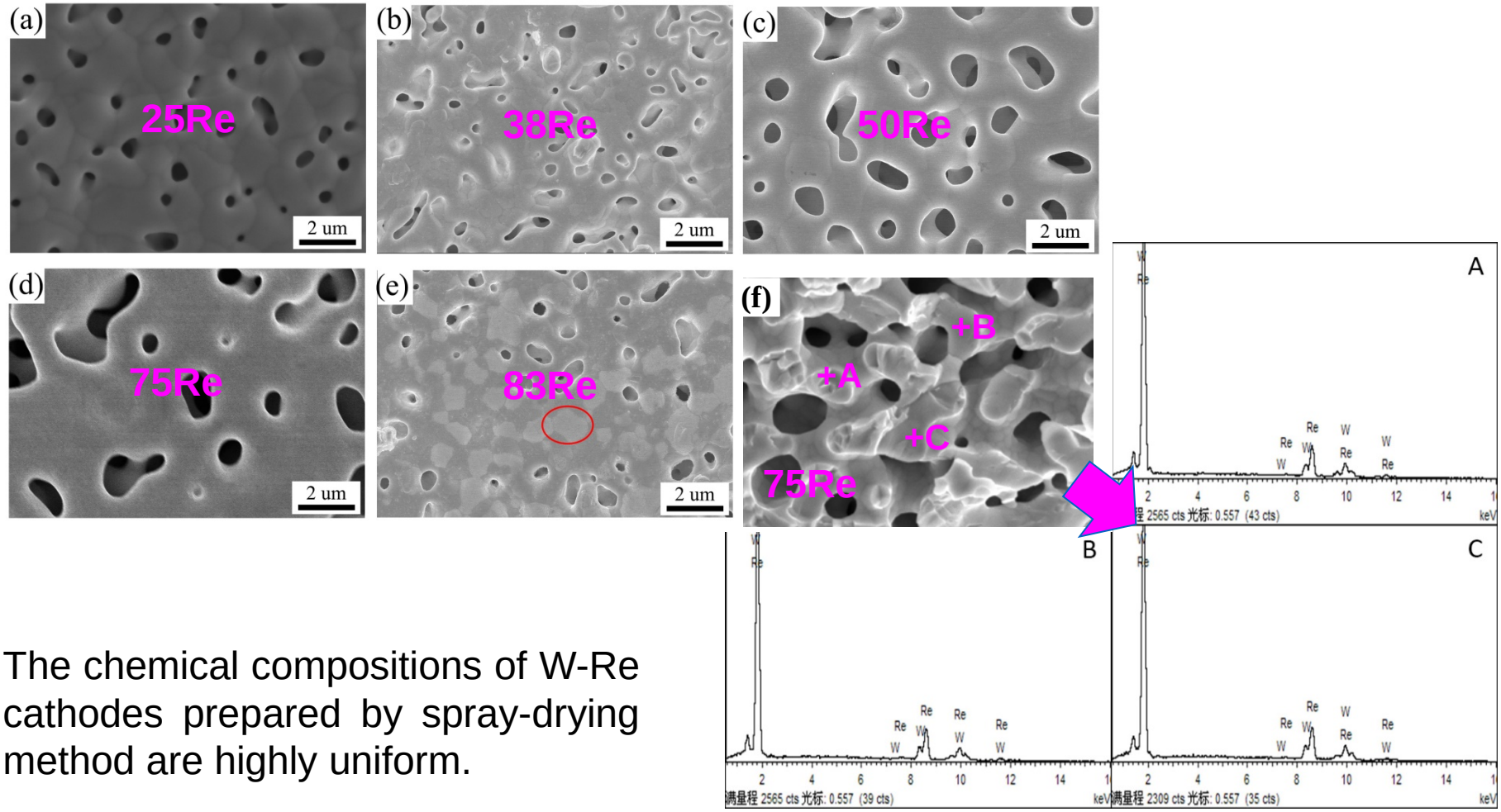




Jinshu Wang, Chen Lai, et al., Chinese Patents: ZL 2014 1 0149295.9

Chen Lai, Jinshu Wang, et al., J. Alloy. Compd. 728 (2017) 984-991.

Sintering of W-Re cathodes



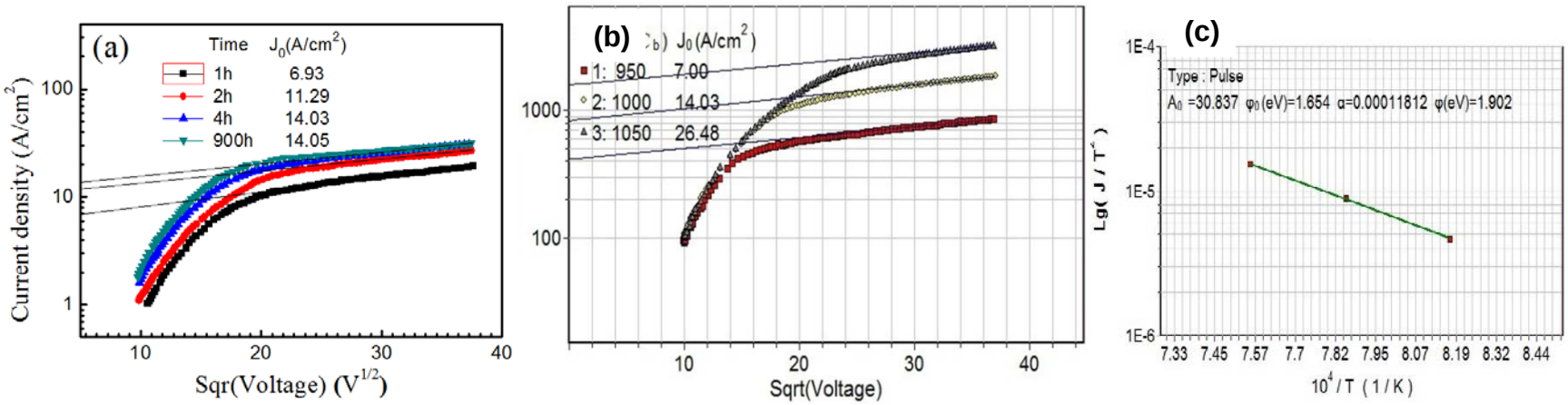
The chemical compositions of W-Re cathodes prepared by spray-drying method are highly uniform.

Chen Lai, Jinshu Wang, et al., J. Alloy. Compd. 728 (2017) 984-991.

Pulse current emission property

Pulse emission current density and work function of W-Re matrices dispenser cathodes

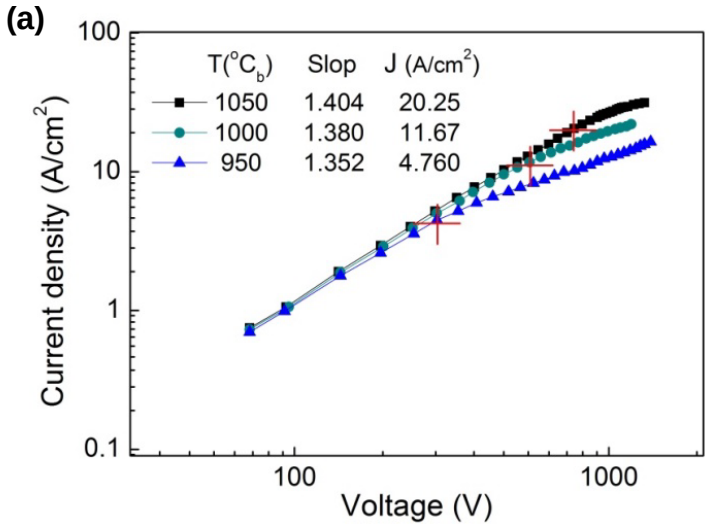
Composition/ Temperature	W A/cm^2	25Re A/cm^2	38Re A/cm^2	50Re A/cm^2	75Re A/cm^2	83Re A/cm^2	Ref.
1100	13.65	20.66	20.66	21.01	/	19.81	
1050	8.13	11.82	11.82	13.46	26.48	12.75	<8
1000	4.8	7.15	7.15	8.52	14.03	8.41	
950	2.74	3.86	3.86	5.03	7.00	4.41	
900	-	1.74	1.74	2.37	-	2.79	
Φ	2.121	2.101	2.084	2.005	1.902	2.051	

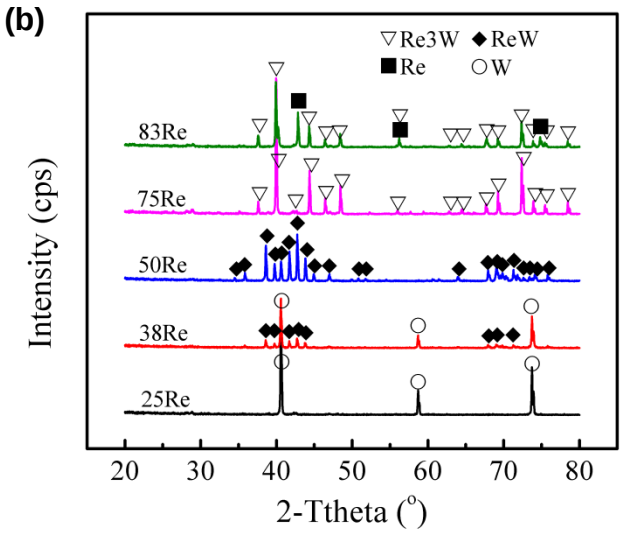


Direct current emission property

Direct current emission density of different cathodes at 1000℃

Sample I.D.	25Re	38Re	50Re	75Re	83Re	75Re [1]
Density (A/cm^2)	2.12	2.56	6.27	11.67	8.58	2.16





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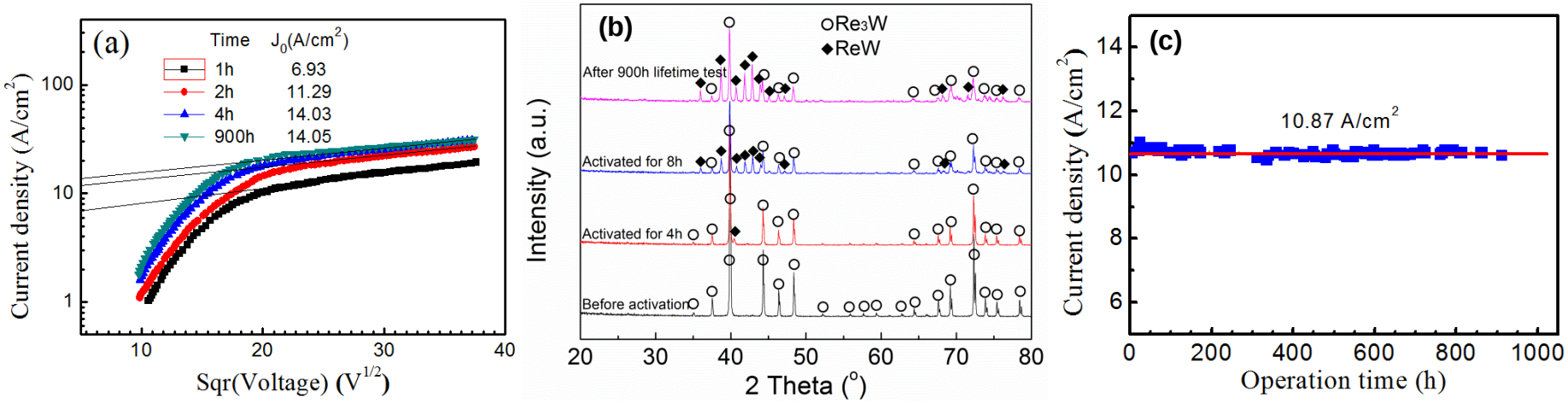
[1] A. Taran, et al. Vacuum Electronics Conference, 2009. IVEC '09. IEEE International, 54, 2009, 1-2.

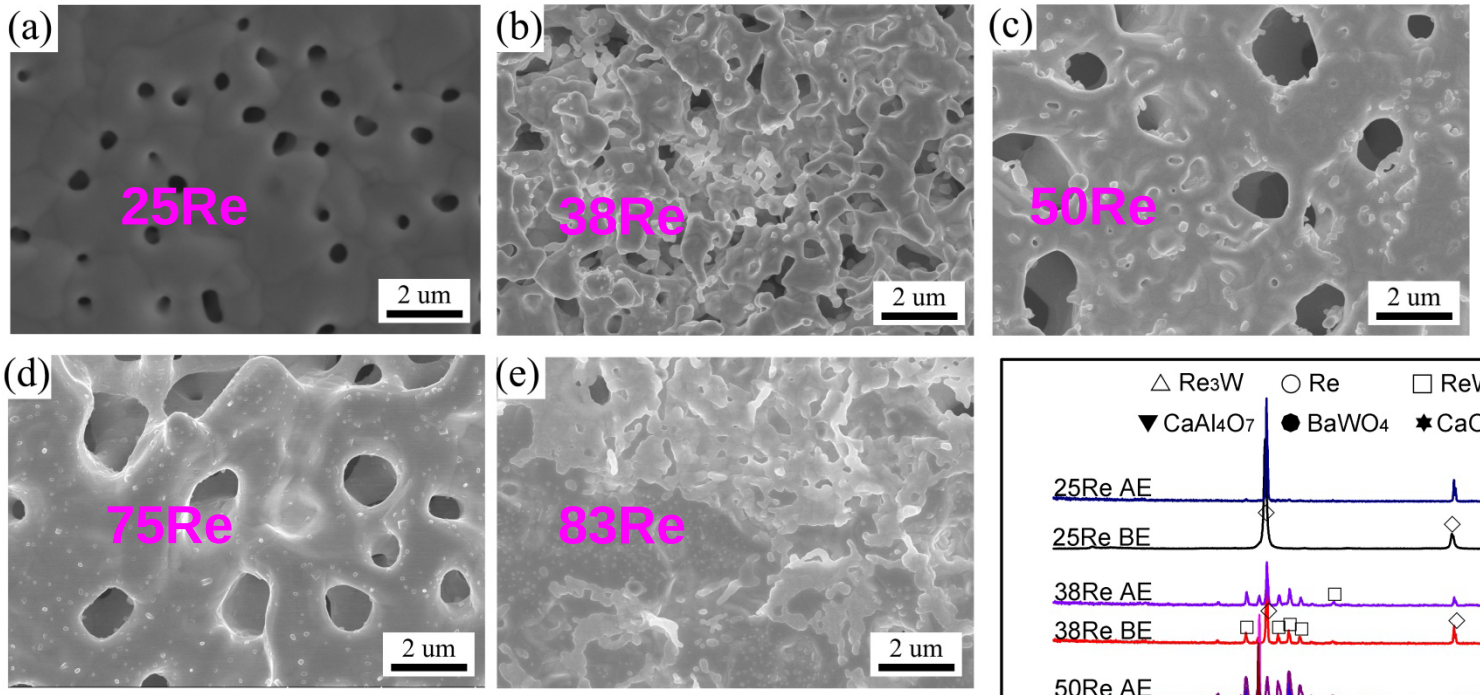
Phase dependent emission property



(a) The pulse emission current density as a function of activation time, (b)The phase transition of W-Re cathodes before and after activation, (c) The 900h lifetime test at 1000℃

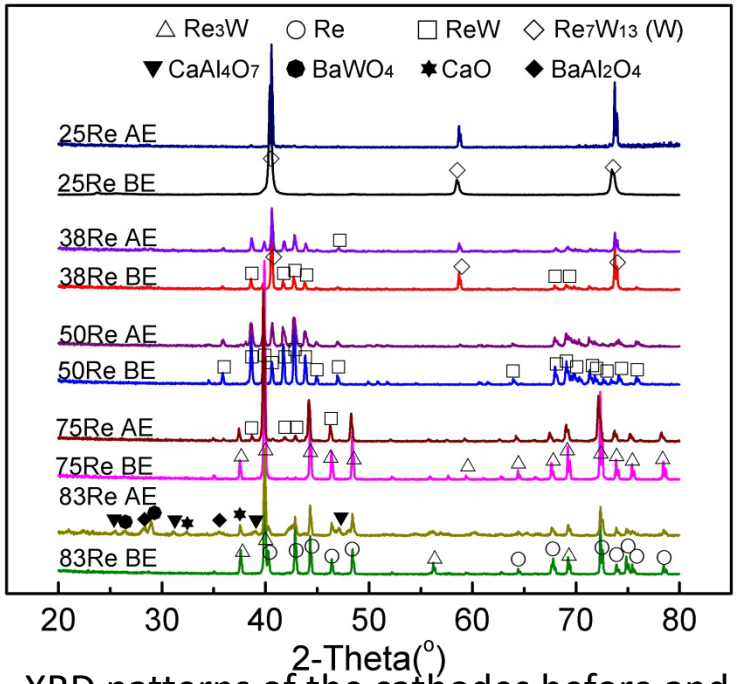
During the lifetime test, the phase transition of W-Re cathodes hardly affects the emission property.

Surface morphology of cathodes

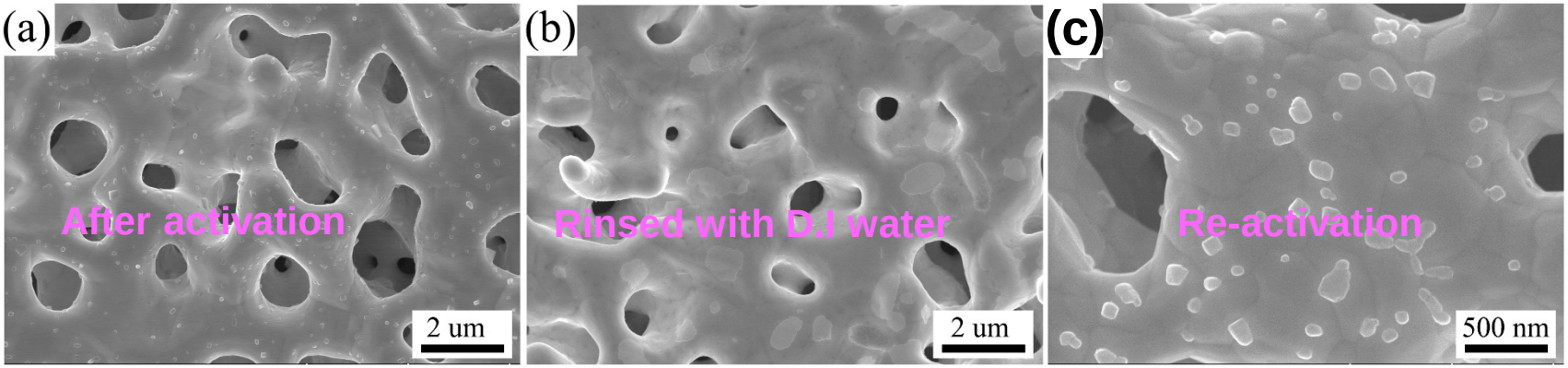


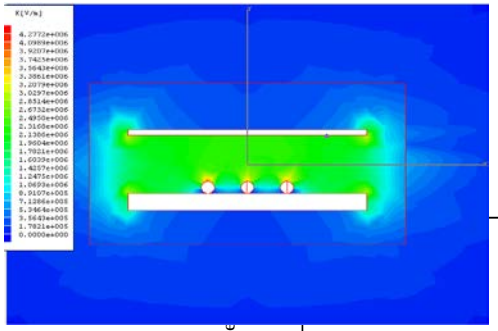
The nanoparticles at the surfaces of 75Re cathodes are related to Re_3W.

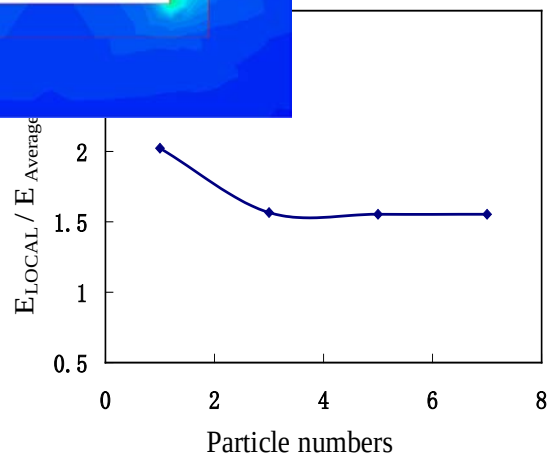
The appearance of agglomerated active slats at the surfaces of 38Re and 83Re cathodes is caused by their complex phase constitutions.

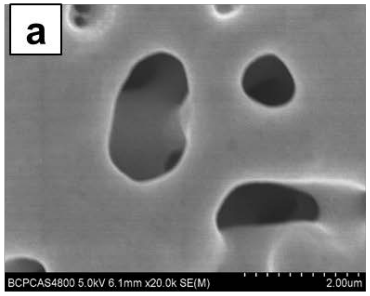


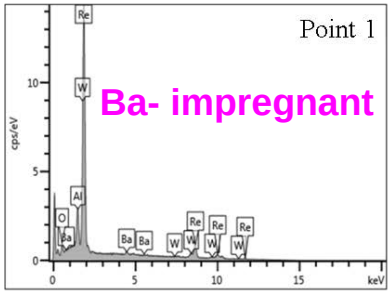
XRD patterns of the cathodes before and after activation.



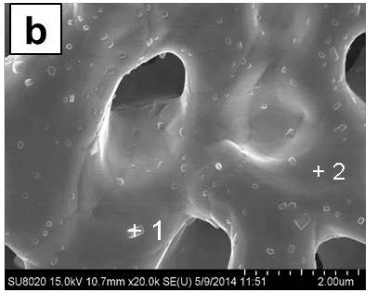


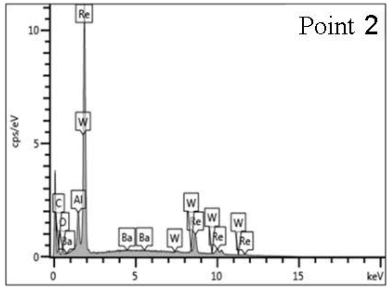






图谱 1	
元素	wt%
O	5.13
Al	3.00
Ba	2.48
W	19.86
Re	69.54
总量:	100.00





图谱 2	
元素	wt%
O	2.77
Al	2.44
Ba	0.62
W	18.19
Re	75.98
总量:	100.00

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Surface composition of cathodes

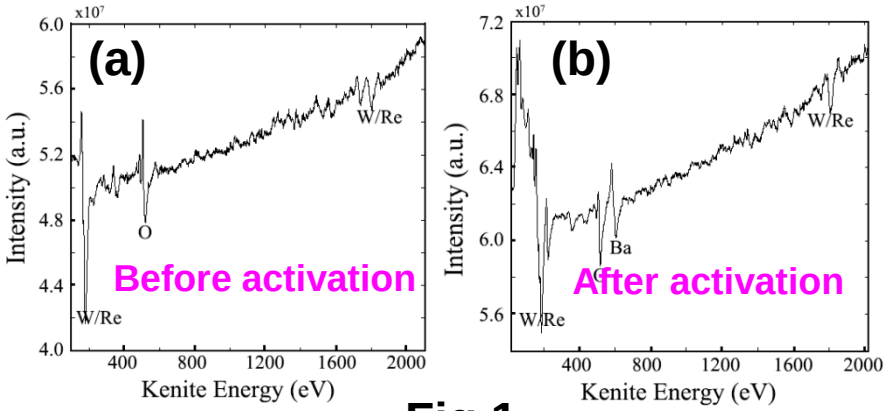


Fig.1

Table Chemical compositions of as obtained cathodes

Elements/ Cathodes	O	Ba	W	Re
W	18	29	53	/
25Re	9	26	43	22
50Re	8	25	35	32
75Re	11	30	24	35
83Re	29.4	47.8	6.7	16.1

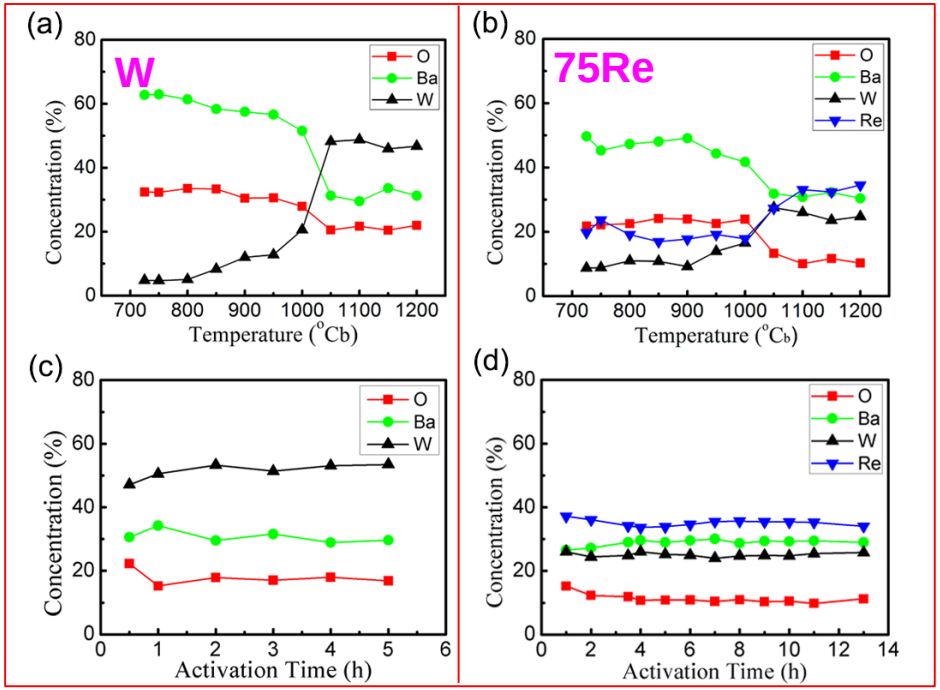


Fig.2

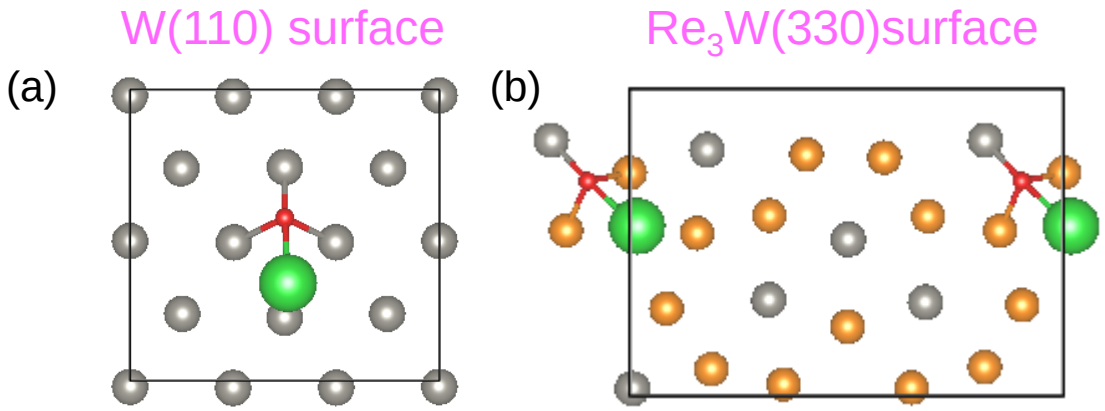
The atomic ratio of Ba:O of the active emission layer is 3:2 and 3:1 in Ba-W and Re-W cathodes, respectively.

Adsorption properties of Ba-O on W and Re doped W

Table The adsorption energy of Ba-O on Re-doped W(011) surface

	W(011)			
Site	W(011)	1Re-W(011)	2Re-W(011)	3Re-W(011)
O	-9.010	-8.781	-8.434	-8.326
Ba	-4.087	-4.234	-4.264	-4.2027
Ba-O	-5.187	-5.104	-4.787	-4.618

Adsorption properties of Ba-O on W and Re3W



The adsorption energies of Ba-O on W(110) and $Re_3W(330)$

Crystal plane	W(110)	$Re_3W(330)$
Site	hollow	hollow
Ba on O-M	-3.783	-4.412
Ba-O	-5.047	-5.234

The adsorption energy of Ba-O on 75Re cathode is higher than the tungsten matrix cathode.

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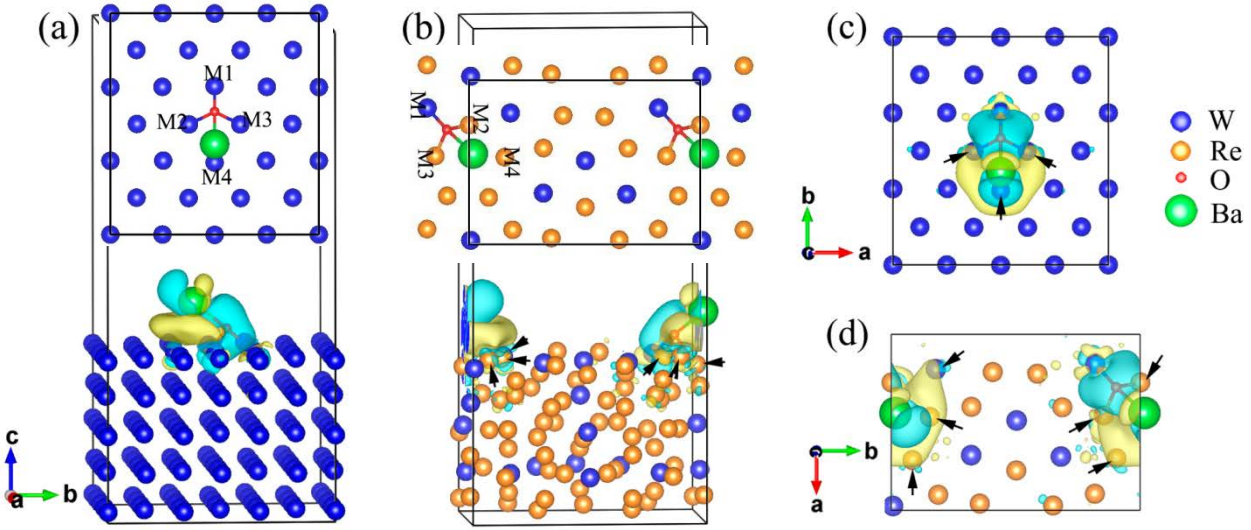
Electron configuation of Ba-O on W and Re_3W



XPS data		
	Ba-W	75Re
W	30.8(M) 31.7 35.3	31.0(M) 31.8 35.3
Re	/	40.05 40.35(M) 41.1
O	530.1 531.6	530.1 531.8
Ba	779.8	779.8

The configuration and electron structure of Ba-O on (a) (c) W(011) and (b) (d) Re3W(330).

Bader-charge analysis (eV)

Atoms	Ba	O	M1	M2	M3	M4
W(110)	-1.28	+1.16	-0.25	-0.08	-0.06	+0.31
$Re_3W(330)$	-1.34	+1.10	-0.62	-0.01	-0.01	+0.48

"-"represents "lose charge"

Improved charge transfer from Ba to the atoms of Re_3W matrix results in a stronger interaction between Ba and W/Re and enhances the absorption of Ba.

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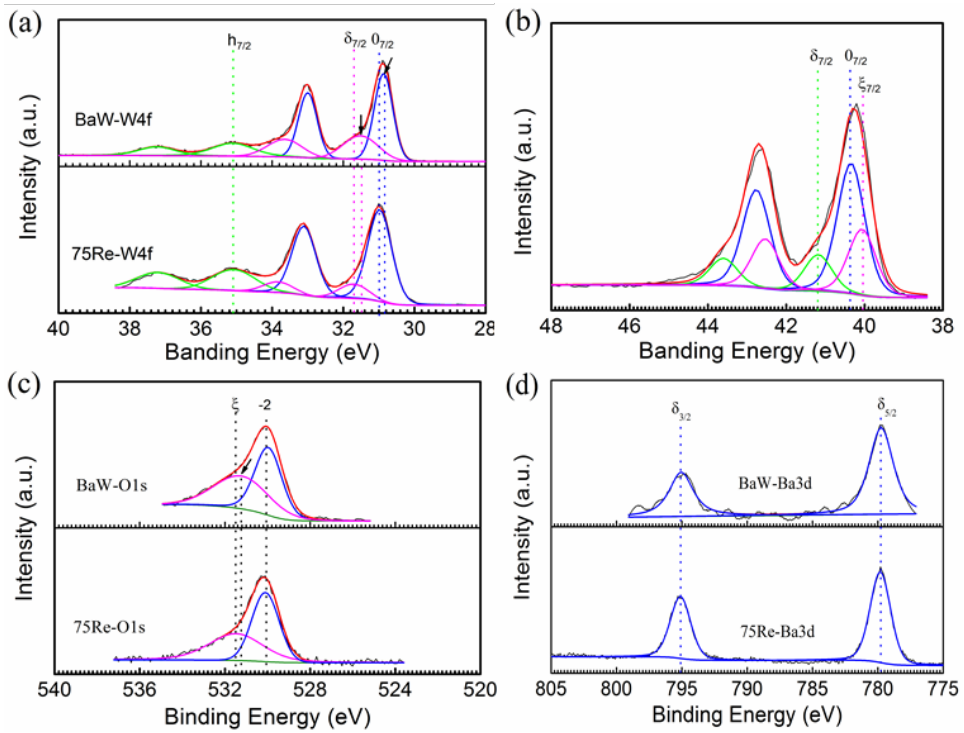
Chemical state of surface elements



	Ba-W	75Re
W	30.8(M) 31.7 35.3	31.0(M) 31.8 35.3
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O	530.1 531.6	530.1 531.8
Ba	779.8	779.8

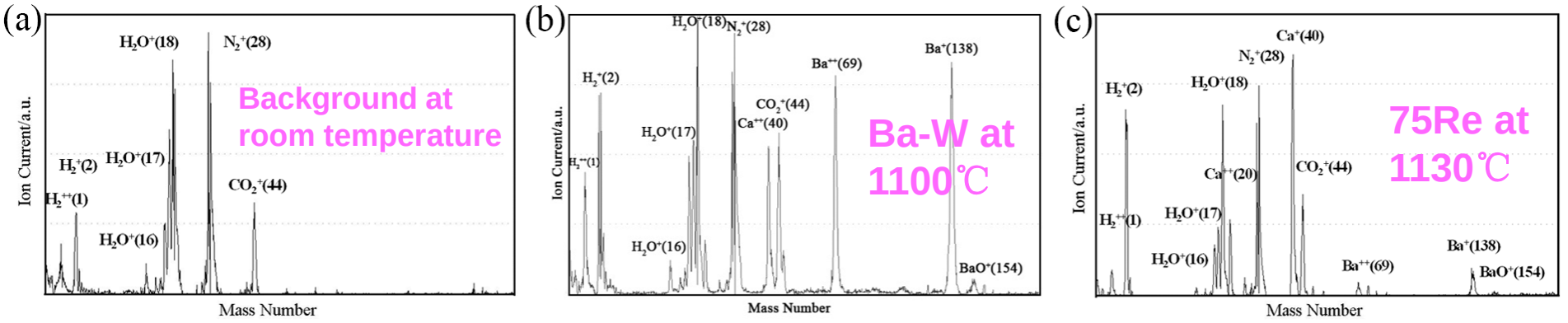
XPS spectra of Ba-W and 75Re cathodes (a) W4f, (b) Re4f, (c) O1s, (d) Ba3d.

Re improves the adsorption ability of Ba rather than involves into the chemical reactions.

Evaporation of active substance at cathode surfaces

Evaporation rate of Ba-W and Re_3W cathodes

	Evaporation rate ($g \cdot cm^{-2} \cdot s^{-1}$)		
Tem. (℃)	1000	1050	1100
Ba-W	$0.333X10^{-8}$	$1.26X10^{-8}$	$3.81X10^{-8}$
75Re	$0.189X10^{-8}$	$0.461X10^{-8}$	$1.15X10^{-8}$



Time of Flight Mass Spectrum

Summary

- scandate cathode with the tungsten matrices prepared by selective laser meltingmethod can provide the emission density of 66 A/cm^2 at 950^{o}C.
- Sc_2O_3-W cathode prepared by microwave sintering can provide the emission density of 40 A/cm^2 at 850^{o}C with the slope of 1.42.
- The 75Re cathode possess the highest electron emission density among as prepared Re-W mixed matrices cathodes. The direct electron emission density of 75Re at 1000 ^{o}C could achieve 11.67 A/cm^2 and kept stable during 900 h lifetime test.
- The addition of Re increases the adsorbability of Ba in W-Re cathodes and enhances the atomic ratio of Ba/O at active layer, resulting in improved emission property.

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Yazhou Hua
……

Thanks for attention!