Temperature Effects on Desorption Behavior and Characteristic Wulff Shapes of Scandate Cathodes

Mujan N. Seif, Thomas John Balk, Matthew J. Beck
Department of Chemical and Materials Engineering
University of Kentucky
Lexington, KY, USA, 40506

Abstract: *Scandate cathodes have been shown to exhibit superior emission properties to other classes of thermionic cathodes. However, a deeper understanding of their fundamental operating behavior is crucial before widespread technological integration. It is a widely held hypothesis that the electron emission of scandate cathodes is related to Ba availability on the surfaces of the porous W matrix. In addition, extensive characterization of scandate cathodes motivates an additional hypothesis that high- performance cathodes all contain W nanoparticles of a particular shape. These attributes, Ba availability and nanoparticle shape, are significantly affected by temperature – the former due to desorption and the latter to the temperature-dependence of surface excess free energies. Here, we report computed Ba desorption rates for surfaces at 850°C (operating temperature). We show that total Ba evaporation from the Ba/O-decorated W(110) surface is ∼13 orders of magnitude higher than the Ba/O- decorated W(112). We also report that temperatures on the order of 850 °C imply that chemical environments sufficient to reduce BaO are required to form the W particle shapes observed in high-performing Sc cathodes.*

Keywords: thermionic cathode; surface excess free energy; scandate cathode; Ba desorption; Wulff shape

Introduction

Scandate cathodes are a high-performing subset of porous thermionic cathodes and are fabricated by impregnating a porous Sc-doped W body in a hydrogen atmosphere with a melt containing BaO, Al_2O_3, and CaO [1]. While scandates exhibit superior emission properties to state-of-the-art thermionic cathodes, it is not currently known exactly how each step of fabrication contributes to improved electron emission. In fact, seemingly identical fabrication processes often yield batches of cathodes wherein some exhibit outstanding properties and others poor. This issue must be addressed before widespread technological integration.

It is a widely held hypothesis that the electron emission of scandate cathodes is related indirectly to Ba availability on the surfaces of the porous W matrix. In addition, extensive characterization of scandate cathodes by Liu *et. al.* [2] motivates an additional hypothesis that high-performance cathodes all contain W nanoparticles of a *particular* Wulff shape (Fig. 1). These attributes, Ba availability and nanoparticle shape, are significantly affected by temperature – the former due to desorption and the latter to surface excess free energies ($\hat{\gamma}$). Here, we report Ba desorption rates for surfaces at 850 °C over 30,000 hours, which is the standard operating temperature and lifetime. We find that total Ba evaporation for the Ba/O- decorated W(110) surface was ∼13 orders of magnitude higher than the Ba/O-decorated W(112), and ∼15 orders higher than a Ba/Sc/O-decorated W(112). We also report the changing stability of Ba/Sc/O-decorated W surfaces as a function of temperature and O_2 availability. We construct "phase diagrams" relating these parameters, then search phase space to find a window wherein the W(110), W(001), W(112) surface excess free energies yield the characteristic W nanoparticle shape present in high-performing scandate cathodes.

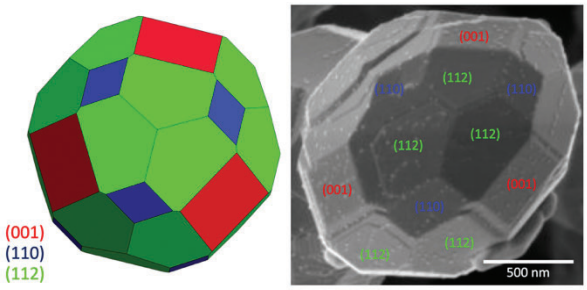

Figure 1. (left) Wulff construction of the equilibrium W grain shape present throughout thermionic cathodes (right) SEM images of a high-performance cathode, always exhibiting a characteristic W grain shape.

Methods

A. Ba Desorption

The desorption rate is computed according to the expression $D = f^*\exp[-\Delta E/k_BT]$, where f is a frequency prefactor computed according to Transition State Theory [3] and the exponent is a Boltzmann factor dependent on the Ba binding energy (ΔE), Boltzmann constant (k_B), and temperature (T).

B. Characteristic Wulff Shape

To accurately compute the surface excess free energies, we incorporate both the electronic and phononic contributions. Traditional DFT calculations only include the former;

hence, surface "energies" generally reported are actually surface *enthalpies*. The electronic contribution was computed with self-consistent VASP calculations. The phononic contribution was found by computing vibrational frequencies of the system according to density functional perturbation theory. These contributions are combined to calculate free energies via the method implemented by Togo *et. al.* [4]. Once the temperature- dependent surface excess free energy was computed for each surface, Wulff shape-T -μ_O phase space is searched until a set of relative surface energies is found which would result in the desired shape.

Results and Discussion

The total desorption for each surface varied tremendously, as shown in Fig. 2. Total Ba evaporation for the W(110) surface was ~12-15 orders of magnitude higher than the two W(112) surfaces included. Considering that the W(112) surface covers ~70% of the surface area in an equilibrium W grain present in high performance scandate cathodes, the near- zero Ba evaporation of the W(112) suggests that thermionic cathodes may not be emitting a substantial amount of Ba.

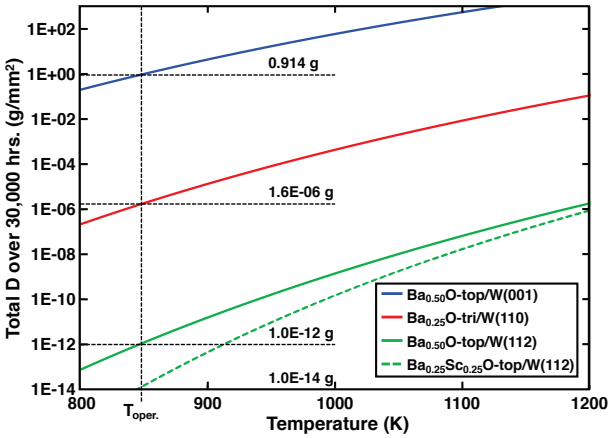

Figure 2. The total Ba desorption from each surface after 30,000 hours as a function of temperature. The total mass desorbed at operating temperature (850 C) is highlighted.

$\hat{\gamma}$ for several surfaces are computed at temperatures ranging from 0 - 2000 K, with the results for 1450 K plotted in Fig. 3. The solid vertical bars indicate the μ_O stability bounds for various oxides present in the system (e.g. to the left of the magenta bar, the Ba is assumed to be in metallic form; on the right, BaO). At temperatures below ~1200 K, we do not observe phase space wherein the relative surface energies yield the characteristic shape. Above that temperature, there exists a narrow μ_O field where the surface energies indeed cooperate (indicated by the gray box and "zoom in" window in Fig. 3). The surfaces comprising this set are bare W(110), Ba/O- decorated W(001), and a Ba/Sc/O-decorated W(112). This is plausible for several reasons. Firstly, the window appears be- tween the black and magenta lines. Since the system contains metallic Ba and Sc_2O_3, it is encouraging that the window appears here. Secondly, the temperatures where the window occurs is less than both activation (1450 K) and operating (1200 K) temperatures. Additionally, the Ba desorption results indicate that the W(110) surface expelled a tremendous amount of Ba, while the W(112) surface evaporated essentially none. Thus, it is plausible that the W(110) surface is indeed bare and the W(112) Ba-containing. The presence of Sc on the W(112) yields insight into a reason that the addition of Sc to thermionic cathodes improves performance – the Sc stabilizes the W(112) facet and produces the characteristic W nanoparticle shape.

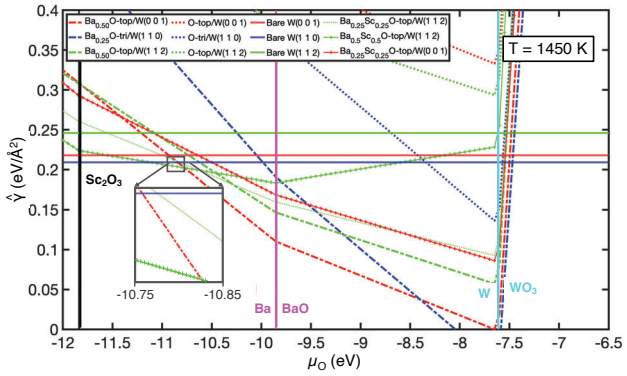

Figure 3. A "phase diagram" relating $\hat{\gamma}$, T, and μ_O. The narrow window wherein in the relative surface energies yield the characteristic shape of high-performing scandate cathodes is highlighted with the gray box and "zoom in" window.

Summary

Temperature effects on Ba desorption and characteristic Wulff shape were reported here. It was found that total Ba evaporation for the W(110) surface was ~12-15 orders of magnitude higher than W(112). Since the W(112) surface covers substantial amount of surface area in an equilibrium W grain, the near-zero Ba evaporation of the W(112) suggests that scandate cathodes may not be emitting a significant amount of Ba. In addition, surface energy calculations indicate that above 1200 K, there exists a narrow μO field wherein relative surface energies cooperate to form the characteristic Wulff shape. The lowest surface energies in this window are bare W(110), Ba/O- decorated W(001), and Sc/Ba/O-decorated W(112).

Acknowledgment

This work was financially supported by the Defense Advanced Research Projects Agency (DARPA) Innovative Vacuum Electronics Science and Technology (INVEST) program, under grant number N66001-16-1-4041.

References

[1] R. Levi, *Journal of Applied Physics*, vol. 24, p.3., 1953

[2] X. Liu *et. al.*, *Materials Characterization*, vol. 148, pp. 188-200, 2019.

[3] L. T. Kong and L. J. Lewis, *Physical Review B*, vol. 74, no. 7, 2006

[4] A. Togo and I. Tanaka, *Scripta Materialia*, vol. 108, pp. 1–5., 2015