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14. ABSTRACT
Funds were requested to purchase an Impedance Analyzer that can be employed to analyze the ion-conductivity of metal oxides. More specifically this instrument was used to measure the oxygen-ion mobility in oxidizers used in advanced nanoenergetic formulations to evaluate if indeed the oxygen-mobility is a major controlling parameter in the ignition temperature of such materials. A better understanding of oxygen transport, and its relationship to energetic material reactivity should enable better design of advance energetic formulations.

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Report Title

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(c) Presentations

Number of Presentations: 0.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

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Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

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FTE Equivalent:	
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Names of Post Doctorates

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FTE Equivalent:	
Total Number:	

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NAME	PERCENT_SUPPORTED	National Academy Member
Michael Zachariah	0.00	
FTE Equivalent:	**0.00**	
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Sub Contractors (DD882)

Inventions (DD882)

Scientific Progress

Technology Transfer

Impedance Spectroscopy Tool for Characterizing Condensed State Ion-Transport in Energetic Formulations

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ABSTRACT

Funds were requested to purchase an Impedance Analyzer that can be employed to analyze the ion-conductivity of metal oxides. More specifically this instrument was used to measure the oxygen-ion mobility in oxidizers used in advanced nanoenergetic formulations to evaluate if indeed the oxygen-mobility is a major controlling parameter in the ignition temperature of such materials. A better understanding of oxygen transport, and its relationship to energetic material reactivity should enable better design of advance energetic formulations.

Equipment Purchased:
Oxygen ion conductivity was measured from the AC impedance analysis using a Solartron 1260 A, shown in Figure 1 (a), by two-point probe electrochemical impedance spectroscopy over the frequency range of 1 Hz to 10^6 Hz with perturbation amplitude of 100 mV. The measurements were performed between 200 and 700 °C or 200 and 750 °C in air. The schematic plot of the sample holder is shown in Figure 1(b).

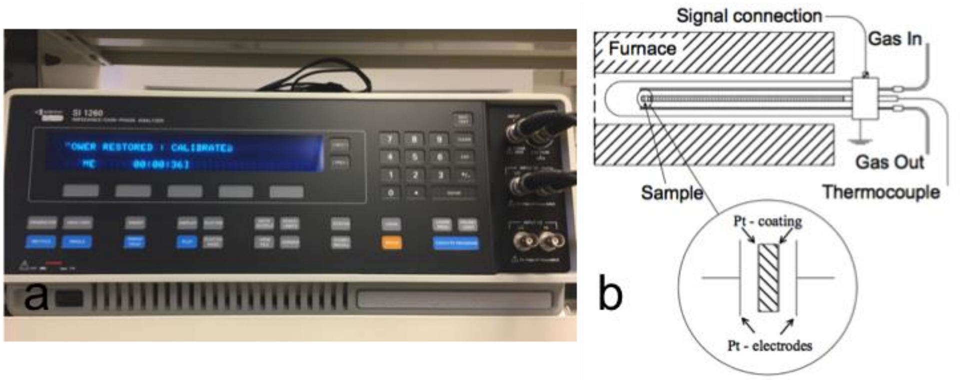

Figure 1. (a) Solartron 1260A Impedance/Grain-Phase Analyzer (b) Schematic plot of sample holder

Figure 2 shows typical impedance spectra obtained for tungsten doped Bi_2O_3 (WSB), as an example, at (a) 200°C and (b) 500°C. The impedance associated with particular transport mechanisms (bulk, grain boundary, surface layer etc.) was assigned by calculating the capacitance [1]. The conductivities were converted from the bulk resistance and the dimensions of the sample based on $\sigma = L/_{RA}$, where σ is the oxygen ion conductivity, R is the bulk resistance, L and A is the thickness and sectional area of the pellets.

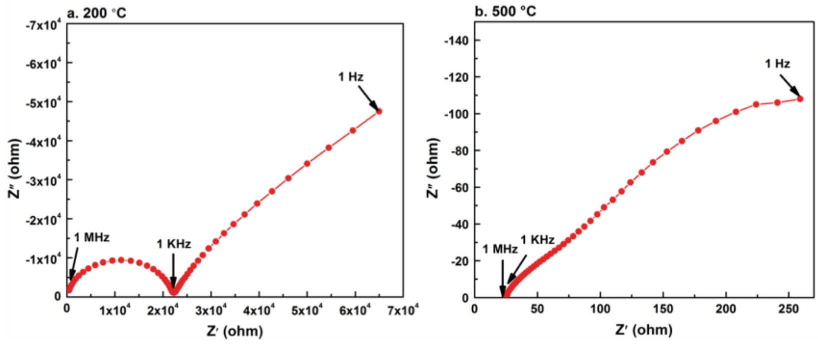

Figure 2. Typical impedance spectra (in this case WSB) in air at: (a) 200 °C and (b) 500 °C.

Nanothermites offer high energy density and high burn rates, but are mechanistically only now being understood. One question of interest is how initiation occurs and how the ignition temperature is related to microscopic controlling parameters. Al-Bi_2O_3 is one of the most interesting thermites for two reasons: The ignition is almost certainly through a condensed phase reaction [2]. The other is that Bi_2O_3 has the highest known oxygen ion conductivity [3], which one might reasonably expect to be an important parameter. In this study, we explored the potential role of oxygen ion conductivity in Bi_2O_3 as a controlling mechanism for condensed phase ignition reaction by employing impedance spectroscopy. Seven different doped δ-Bi_2O_3 with a constant dopant ratio of 15mol% and pure Bi_2O_3 were synthesized by aerosol spray pyrolysis. The ignition temperatures of Al/doped Bi_2O_3, C/doped Bi_2O_3 and Ta/doped Bi_2O_3 were measured by temperature-jump/time-of-flight mass spectrometer coupled with a high-speed camera respectively. These results were then correlated to the corresponding oxygen ion conductivity for these doped Bi_2O_3 measured by impedance spectroscopy between 200 and 750 °C.

Figure 3 (a) shows an Arrhenius plot of the bulk ionic conductivity of doped Bi_2O_3, showing, as expected, an increase in ion-conductivity with temperature. The conductivities in the region of ignition temperature are shown with more detail in Figure 3(b).

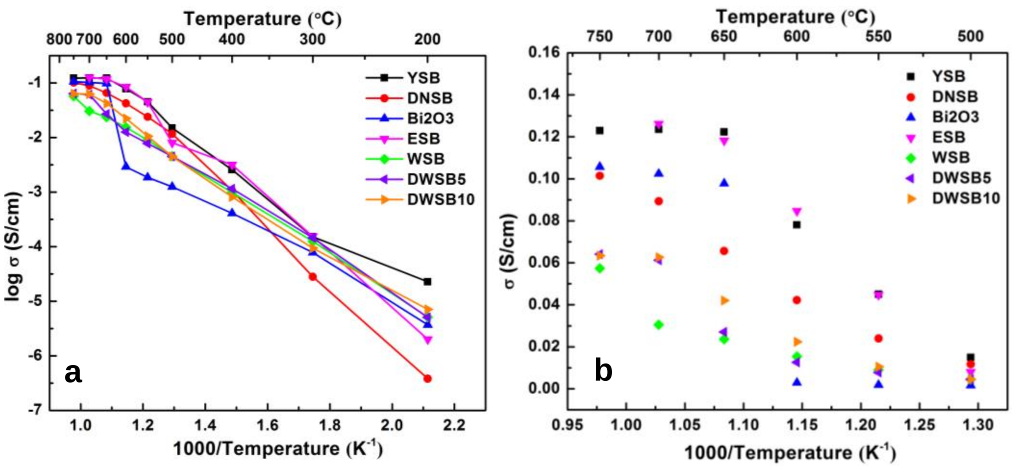

Figure 3. (a) Arrhenius plot of measured ion-conductivities for doped Bi_2O_3. (b) Zoomed in measured ion conductivities at 500-750 °C for doped Bi_2O_3

Based on Figure 4, we note that three different fuels (Al, C and Ta) with very different physical-chemical properties are observed to have essentially equivalent critical oxygen ion conductivity for the ignition of doped Bi_2O_3 oxidized thermites, as long as aluminum is molten. Noting that ignition temperature is varying, but the oxygen ion conductivity at ignition is constant, even though conductivity is temperature sensitive as seen in Figure 3, we may conclude that there exists a critical oxygen ion conductivity (~0.06 S/cm) that controls the ignition of Bi_2O_3 based thermites.

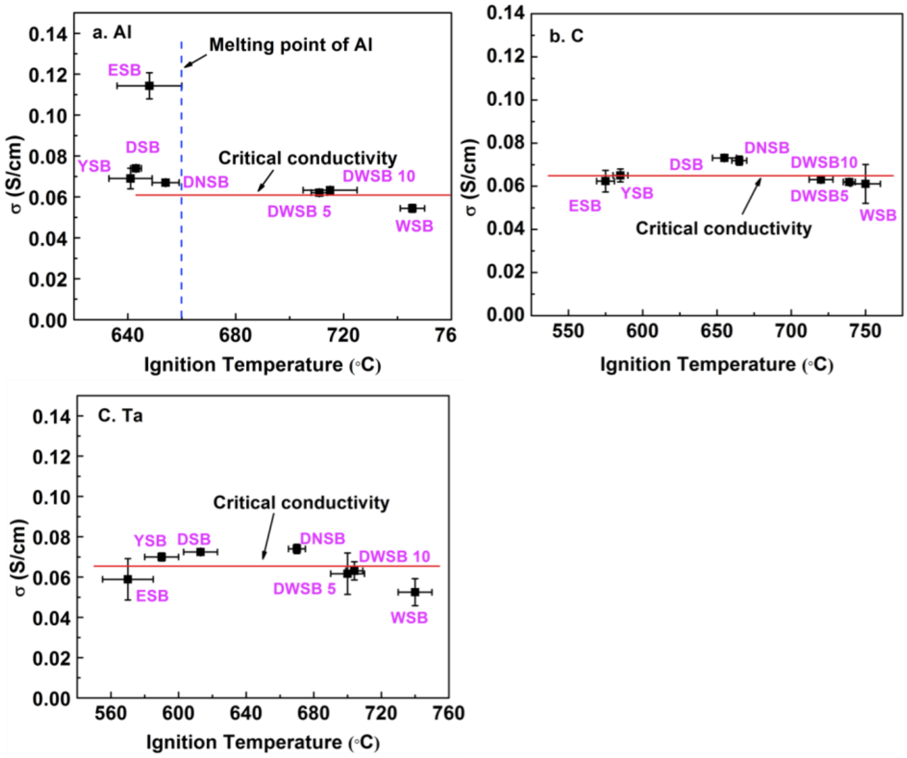

Figure 4. Oxygen ion conductivity as a function of corresponding ignition temperature for (a) Al/doped Bi_2O_3, (b) C/doped Bi_2O_3 and (c) Ta/Bi_2O_3

In Summary, By measuring the ionic conductivities as a function of temperature of seven doped Bi_2O_3's with the same crystal structure and morphology, and their corresponding ignition temperatures with three fuels (Al, C, Ta) respectively, we found a critical oxygen ion conductivity exists for Bi_2O_3 oxidized thermite ignition as long as aluminum is molten. This result suggests that it is possible that oxygen ion initiate condensed phase thermite ignition. To our knowledge, it is the first time that oxygen ion conductivity correlated with condensed phase ignition temperature.

Reference:

[1] J. T. Irvine, D. C. Sinclair, and A. R. West, *Adv. Mater*, **2(3)**, 132 (1990).
[2] N. W. Piekiel, L. Zhou, K. T. Sullivan, S. Chowdhury, G. C. Egan, and M. R. Zachariah, Combust. Sci. Technol **186(9)**, 1209 (2014).
[3] S. Boyapati, E. D. Wachsman, and N. Jiang, Solid State Ionics **140(1),** 149 (2001).