



Transition to electronic conduction at the onset of flash in cubic zirconia

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ABSTRACT

We report *in-situ* measurements of impedance spectroscopy during flash experiments with single crystals of cubic-yttria stabilized zirconia, conducted in ambient air at 300 °C to 700 °C under a direct current electric field. Platinum electrodes transition from blocking to non-blocking behavior before the onset of flash, indicating a transition to partial electronic conductivity during the incubation period. Even though the conductivity continued to increase with temperature the electron transport remained at a plateau of approximately 0.25. This result has ramifications not only in the fundamental understanding but also in technological significance of the flash phenomenon.

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The flash experiment is distinguished from spark plasma sintering, where graphite dies are used to heat and to impart current into the specimen. Here electrical field and current are applied directly to the specimen while the heating is provided by a conventional furnace.

In the original paper [1] the experiments were carried out by applying a field to the specimen and heating it at a constant rate. The onset of flash was signaled by an abrupt rise in the conductivity of the specimen. Arrhenius plots of the electrical power expended in the specimen showed a nearly vertical rise with the onset of flash. The flash temperature fell as the field was increased. Rather surprisingly, the power density at the flash transition remained independent of the applied field. Explanations that invoke Joule heating argue that the Arrhenius increase in ionic conductivity produces this non-linear behavior leading up to flash sintering [2–4]. However, this argument does not explain why the transition is so abrupt and why it occurs at a specific value of the power density, not only for zirconia but nearly universally, for many ceramics [5].

A second way of doing the experiment is to apply the field as a step function while holding the furnace at an isothermal temperature. In this case the instability occurs after an incubation time, which has been called Stage I of the flash experiment [6]. The incubation time becomes quicker if the either the field or the furnace temperature are increased. In both instances (constant heating rate and isothermal experiments) the power surge in the specimen is controlled by switching the power supply to current control; thereafter the specimen can be held in a steady state of flash under current control, also called Stage III. The present work is concerned with *in-situ* impedance spectroscopy during Stage I, before and during the cusp of the rising conductivity in the

specimen, and when very low current densities, $<15 \text{ mA mm}^{-2}$, that is much lower than the current limit used in flash sintering experiments [6].

Joule heating models assume that the conductivity mechanism remains unchanged during the flash transition; for example it is assumed yttria stabilized zirconia (YSZ) remains an ionic conductor [2–5]. An alternative hypothesis for explaining the non-linearity is an avalanche of Frenkel defects and electron-hole pairs, where charge neutral vacancies and interstitials promote sintering and the electron-hole pairs promote electrical conduction [7], and electroluminescence [8]. If this approach has value then an ionic material such as YSZ should also become at least a partial electronic conductor during the flash transition. In the present work we employ *in-situ* impedance spectroscopy to show that YSZ does indeed transition to mixed ionic and electronic conductivity as the flash transition is approached. What is remarkable is that this transition begins during the incubation period before the cusp of the increase in conductivity, suggesting that it may have a fundamental role in the onset of the flash.

There have been recent reports by West and coworkers of electronic conductivity in yttria stabilized zirconia (YSZ) with a DC bias [9–11]. Impedance spectroscopy has shown that the conductivity transitions from ionic to mixed ionic and electronic behavior [9], leading to the speculation that a similar effect may be expressing itself during flash experiments.

There is another example of electronic conductivity in zirconia under a DC bias. In 1992 Wagner et al. [12] have reported experiments with cells made from cubic yttria-stabilized zirconia sandwiched between nickel-metal electrodes. The experiments were carried out at 927 °C, at a residual pressure of 10^{-3} Pa (10^{-8} atm) at a current density of 40 mA cm^{-2} . The conduction mechanism, at this temperature, in doped zirconia remains ionic within the oxygen pressure range of

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10^{-20} to 10^{10} atm [13]. Thus it was expected that the electrolyte would have behaved as an ionic conductor.

When current was passed through, the voltage, expressed across the cell, quickly declined presumably due to an unexpected increase in conductivity, similar to the flash phenomenon. Electron microscopy of the interfaces, on either side of the electrolyte, revealed that nickel oxidized into nickel-oxide at the anode, while the electrolyte was reduced and reacted with nickel to form a nickel-zirconium intermetallic at the cathode. The cross-sectional images of the growth of the nickel-oxide layer were used to calculate the number of oxygen ions transported across electrolyte. At the same time the Faraday charge transported during the experiment was measured by integrating the current with time. It was discovered that oxygen ions could account for only 5% of the total charge transported through the cell, leading to the conclusion that charge transport through the electrolyte was partially electronic.

In this letter we describe *in-situ* impedance measurements during the flash transition, in real time, to divulge whether or not there is an onset of electronic conductivity during the early stages of the flash experiments. The present work covers the period which begins before and extends slightly into the cusp of the rising current, also called Stage I. The experiments are carried out at 100 V cm^{-1} applied to the specimen while the furnace temperature was raised in a stepwise fashion. In this way the onset of electronic conductivity could be detected before and during the flash transition.

The experiments were carried out with an impedance analyzer, Agilent Technologies, CA, USA, which has a built in DC bias capability, although with the current limited to low values. The current limit was not an issue since our objective was to study the early stage of flash onset, much below the limit generally used in flash sintering experiments [7]. The current through the specimen was measured by the voltage expressed across a 30Ω resistor placed in line with the sample in the DC circuit. This resistor is nearly one hundred times smaller than the resistance of the sample that we would measure during flash; therefore it does not introduce any significant error in the impedance calculation. The current in the circuit was then obtained by dividing the measured voltage (with Keithley 2000) by 30Ω . In addition a second multimeter, also a Keithley, measured the DC voltage immediately across the specimen during the live experiment.

Single crystals of cubic phase of 8 mol% yttria stabilized zirconia with (100) orientation were used in this study [14]. The crystals were cut into parallelepiped shaped specimens, and polished to length, width, and thickness of 3 mm, 1 mm, and 0.5 mm, respectively. The ends of sample were wrapped with thin platinum wires, leaving a gage length of 1 mm on the sample. Platinum paste was applied to the wrapped wire to ensure electrical contact with sample. The samples were placed within

the horizontal furnace (Applied Test System, PA, USA) suspended by the platinum wires that also carried DC field to the specimen.

The impedance was measured while a DC voltage, corresponding to a field of 100 V cm^{-1} , was applied to the sample. The furnace temperature ranged from 300°C to 750°C , and was increased in steps of 50°C . The sample was held at each step for 10 min to stabilize the temperature. The scan time for the impedance spectra was one minute. At each temperature, the experiments were conducted in the ON-OFF mode with and without the electrical field.

The measurement of the current flowing through the specimen across the full range of temperature is given in Fig. 1(a). The power density, equal to the product of the current density and the (concurrently measured) electrical field, is also shown. Note the current density remains below $\sim 15 \text{ mA mm}^{-2}$. Francis et al. [6] have shown that full sintering requires nearly 100 mA mm^{-2} , therefore the experiment was in the very early stages of the flash experiment. Interestingly the cusp in the power density is $\sim 20 \text{ mW mm}^{-3}$, which lies within the band of power density where several oxides have been shown to transition into the state of flash [5]. The formal onset flash temperature, determined from the asymptotes to the power density curve before and after the flash onset, as seen in Fig. 1(a) was $\sim 675^\circ\text{C}$.

The onset of electronic conductivity is discerned from the Nyquist plots of the complex impedance. The semicircle at low frequencies with a large radius represents the very high resistance of the platinum-ceramic interface, which is blocking for the transfer of oxygen ions. However, when the DC field is turned on, the interface resistance immediately falls to negligible value: the platinum electrode becomes non-blocking (please see Supplementary Material for further discussion of this point). The inference is that platinum interface becomes transparent to the transport of electrons. The Nyquist plot at 400°C shows some evidence of a decline in the interface resistance, but at 500°C and above the interface resistance becomes negligible. Note that the semicircle at high frequencies measures the total conductivity of the electrolyte. The radius of the semicircle decreases in the ON state because the total conductivity is now the sum of the ionic and the electronic conductivity. This scenario can be represented in a lumped circuit by two resistors in parallel, one representing the ionic and the other electronic conductivity. Since the ionic conductivity is known from the measurement without the DC field the parallel resistor model yields a quantitative estimate of the electronic conductivity.

Arrhenius plots of the ionic and total conductivity are given on the right in the graphical abstract. The activation energy is $\sim 1.4 \text{ eV}$ before the flash transition and ~ 1.1 within the flash condition. Literature values for the activation energy for oxygen ion conduction in yttria stabilized zirconia range from 0.8 to 1.3 eV [15,16].

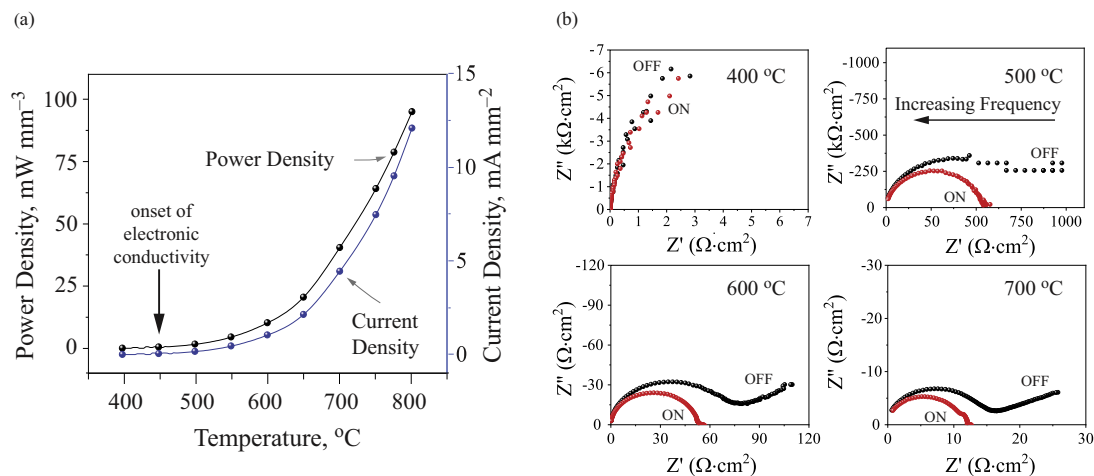


Fig. 1. (a) Change in the current density and the power expended in the specimen under DC field during *in-situ* impedance spectroscopy. (b) Impedance spectra obtained with and without the electric field at different specimen temperatures.

The current profile in Fig. 1(a) falls into two regimes: the first above 600 °C, where the specimen is entering the state of flash, and the second below is 550 °C where the increase in current is incipient and muted. Nyquist plots for experiments at 450 °C, which lies well below the onset temperature are shown in Fig. 2. The current density in these on-off plots with a cycle time of 200 s is shown in Fig. 2(a). The Nyquist plots for the off states and for the on states are shown in Fig. 2(b) and (c) respectively. Clearly even at 450 °C, which is well within the incubation time, the specimen has become a partial electronic conductor. The implication is a transition to partial electronic conductivity may play a role in the development of the flash state. Note that there is some increase in the current with every cycle, also seen by the reduction in the semicircle representing the conductivity of the electrolyte in Fig. 2(c). We believe this represents a characteristic of the incubation time during which the conductivity increases gradually at a constant applied field, eventually precipitating the flash.

The real part of the impedance in Fig. 2 is written in units of area specific resistance (ASR), which is equal to the measured resistance multiplied by the cross sectional area of current flow across the specimen. The resistance of any electrode assembly is now determined by dividing ASR by the cross-sectional area of that electrode.

The electron transport number, t_e , is given by the electronic conductivity divided by the total conductivity of the ceramic. Since it is a normalized quantity it can be calculated from the resistance values in the Nyquist plots. If R_i is the ionic resistance measured with the field-off, and R^* is the total resistance during field-on, then the lumped circuit model leads to

$$t_e = \frac{R_i - R^*}{R_i}$$

Here it is assumed that the ionic portion of the conductivity is not influenced by flash. If it is increased during flash then the value for t_e would be the upper bound value for electron conduction.

The electron transport number obtained in this way for several temperatures is plotted in Fig. 3. Note that it jumps from negligible values to about 0.25 near 450 °C and then continues near this value as the temperature is increased. The numbers in the graph give the values for standard deviation for the data obtained from six experiments. Most notable is that the standard deviation is large near the transition (450 °C) but becomes small well into the flash.

In summary, the key feature of Fig. 3 is that conduction becomes significantly electronic well before the cusp of the flash transition, during the incubation time.

The data for the capacitance in the on-off states at three temperatures, one before the onset of electronic conductivity (at 350 °C) and the third well after electronic conductivity comes into effect (at 600

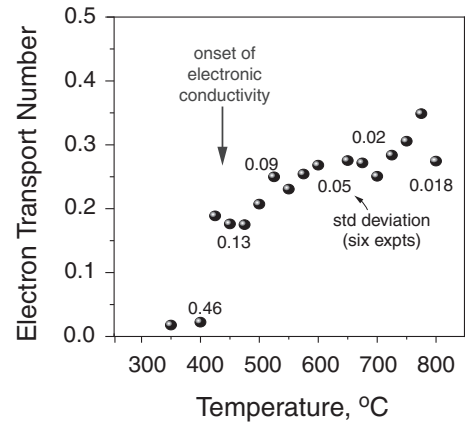


Fig. 3. Electron transport number measured during in-situ impedance spectroscopy as a function of temperature. The standard deviation is measured from six experiments. Note that the variability is higher near the transition to electronic conductivity.

°C) are shown in Fig. 4. The capacitance plots for on and off states are similar at the low temperature, but diverge at high temperature. Normally one expects two plateaus in the capacitance plots, a higher interface plateau at low frequencies and a lower ceramic-matrix plateau at the high frequencies. For the on-state at 600 °C we note a continuous plateau at $4 \times 10^{-9} \text{ F cm}^{-1}$, which merges with the high frequency, ceramic-matrix plateau. This result is to be expected since the interface element is short circuited by electronic conductivity, leaving the lumped circuit with just the matrix element. As such, we now expect to measure only the matrix capacitance, which is indeed the case.

The models for electronic nature of the conductivity in zirconia, induced by flash, have been attributed to polarization, which is initiated at the electrode interface and then propagates as a front into the ceramic. Oxidation of O^{2-} into O^- is assumed to create electronic conductivity [9,17–19]. In one case the position of this “virtual” interface is placed at the edge of a large grain growth front which is itself modeled on the basis of a change in the oxygen state-of-charge [20].

The present experiments add some grist to the mill. In particular they point to two issues: (i) the flash behavior needs to be separated into different regimes of time, current density and temperature, and (ii) the time dependency of flash during the on-off experiments which is apparently very fast needs to be reconciled with the interface polarization models.

To the first point, we did not see any blackening near the electrodes because the current densities were low, but we do observe it in other experiments but only at very high current densities. To the second point a number of on-off experiments of flash have been published

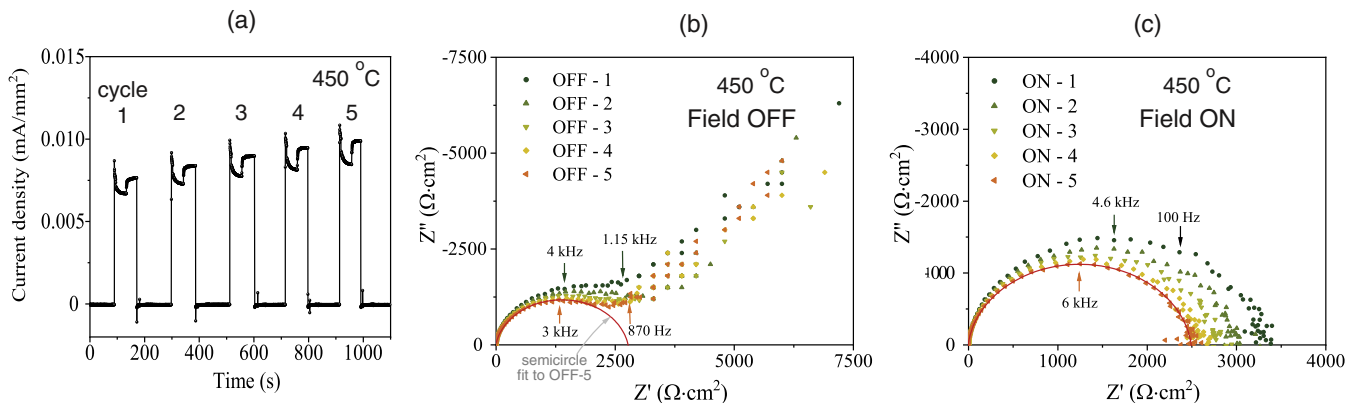


Fig. 2. (a) The change in current density when the field is switched on and off for 5 cycles. (b) In-situ impedance spectra for the OFF periods of the cycle. (c) In-situ impedance spectra for the ON periods of the cycle; note the abatement of the interface resistance.

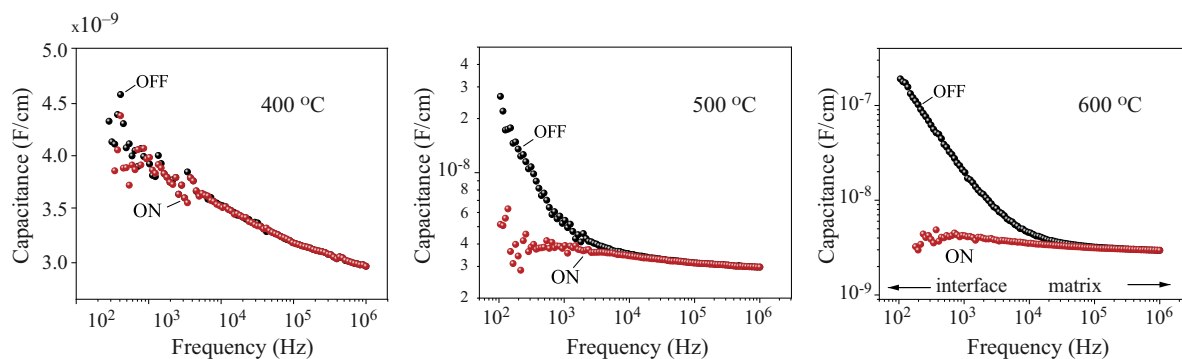


Fig. 4. Plots of specific capacitance from in-situ impedance spectroscopy before (400 °C) and after the onset of electronic conductivity.

from this laboratory which suggest that the relaxation time for initiating and extinguishing the flash effect can be short, as in Fig. 2. A promising start has been made by analyzing the incubation time that leads up to flash [18]. However, the rapid on-off cycling of flash experiments requires an understanding of the generation and recombination of defects on a different time scale [21]. Again, it is important to recognize that flash spans different regimes of behavior in the time/temperature/electric-field/electric-current space.

There could be significant applications of a mixed ionic-electronic state in zirconia. The deployment of zirconia as a free standing membrane for oxygen separation requires some electronic conductivity to prevent the build-up of reverse electrical field by the accumulation and depletion of electrons at the two electrodes. Mixed ionic and electronic conductivity can overcome this limitation by nulling the electrical field. The overall oxygen ion transport will then be controlled by ionic or electronic transport, whichever is slower.

The electronic transition can affect the wetting angle of metals on ceramics which are nominally ionic or covalent. A change in the wetting angle can create surface tension forces which spontaneously draw in the molten metal into the ceramic scaffolding during processing of metal-matrix-ceramic composites.

A third application is that flash activation can limit the open circuit voltage in solid oxide fuel cells prepared with ultrathin electrolytes of YSZ (which is often lower than the ideal Nernst potential). *In-situ* flash can short circuit the electrolyte and reduce the voltage to the field just below the threshold for flash [22].

Recent work that reports an enhancement in the catalytic activity of strontium titanate after flash may also be a result of the change in the electronic structure induced by flash [23].

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Appendix A. Supplementary Material

Supplementary Material to this article can be found online at <https://doi.org/10.1016/j.scriptamat.2019.07.043>.

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