



Flash sintering of ionic conductors: The need of a reversible electrochemical reaction



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ABSTRACT

Flash sintering (FS) is a current-assisted sintering technique able to densify ceramics in short periods of time (just a few seconds) at temperatures significantly lower than in conventional sintering processes. FS technique was firstly reported for yttrium-stabilized zirconia and later it had been proved successful for a large range of oxide materials that present ionic conduction by oxygen vacancies. This paper describes the use of FS on a sodium ion conductor based on a model compound, the beta-alumina. Different electrode materials have been tested, i.e., silver and platinum. The impact of the electrode reaction on the current flow, and thus, on the sintering efficiency is shown for the first time. It appears that the densification by FS can only be possible if the current collectors, i.e., the electrodes, are specifically designed to enable reversible electrochemical reactions at the interfaces between the electrodes and the ionic compound, insuring the current flow through the powder compact.

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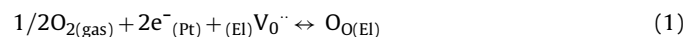
1. Introduction

Flash sintering (FS) is an Electrical Current Activated Sintering technique (ECAS) known for promoting full densification in less than 10 s at significantly lower temperatures compared to conventional sintering techniques [1,2]. Since no die is used, the current mandatorily passes through the sample and the flash process is characterized by an abrupt increase in the sample's conductivity accompanied by shrinkage and densification [1].

It was firstly reported in 2010 for tetragonal yttrium-stabilized zirconia [1] and later it has been extended successfully to a large range of oxide materials such as cubic zirconia [2–4], TiO₂ [5], SnO₂ [6], Y₂O₃ [7], Co₂MnO₄ [8], (La,Sr)(Co,Fe)O₃ [9], ZnO [10], Mg-doped Al₂O₃ [11], phase-mixtures of Al₂O₃ and zirconia [12] as well as for non-oxides as SiC [13].

Published data about FS concerns mostly well-known oxygen vacancy conductors or occasionally electronic and mixed oxygen

vacancy/electronic conductors. For this type of charge carriers, platinum is usually used as a standard electrode material. In this case, a reversible electrochemical reaction (Eq. (1)) occurs at the interface between the powder compact and the platinum current collector (CC) according to:



where gas, Pt and El stand for gas phase, platinum CC and ceramic electrolyte, respectively. Indeed, zirconia ceramics with platinum electrodes in air atmosphere present a reversible and very fast electrode reaction at temperatures higher than 800 °C [14]. This electrochemical reaction allows the current to flow through the powder compact leading to the sample's heating by Joule effect and the FS event.

Despite the emerging interest in the field, nothing has been done, to our knowledge, about FS of non-anionic conductors. However, cationic conductors (Li⁺ or Na⁺ ion), as for example beta-alumina [15,16] and LiSICON [17,18], are very promising materials in the “hot” field of energy storage, and especially, in the case of solid-state batteries which present interesting characteristics in terms of safety and energy density.

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In conventional sintering of beta-alumina, high temperatures (above 1600 °C) are necessary to obtain dense electro-ceramic. Unfortunately, at such high temperatures, a partial decomposition of the beta-alumina is observed due to sodium losses [15]. Therefore, a fast sintering at low temperature, such as enabled by the FS, would be very interesting to preserve the beta-alumina composition and its properties, opening many perspectives of application.

However, when charge carriers are cations such as Li^+ or Na^+ , the electrode reaction with oxygen using platinum as CC as described in Eq. (1) is no longer possible. In contrast, silver ions are well known for their ionic exchange with sodium ions in beta-alumina, which is the main route for synthesis of Ag-beta-alumina [19–22]. Therefore, the possibility of Ag^+ solubility in beta-alumina could make silver metal a suitable electrode material for beta-alumina FS.

In this work, we describe the use of the FS technique on beta-alumina. Moreover, the impact of the electrode reaction using platinum or silver CCs on the FS success is shown for the first time in the literature.

2. Experimental

2.1. Sample processing

Beta-alumina raw powders, of composition $\text{MgNa}_2\text{Al}_{10}\text{O}_{17}$, were prepared via resin synthesis (adapted Pechini's method), which consists in the complexation of metallic cations throughout the extension of a polymer chain formed by polyesterification of ethylene glycol and citric acid. After repeated calcinations at 450, 650 and 1250 °C, the powder was milled to reduce the agglomerates size. After milling, a specific surface area of 21 g/m^2 was determined by BET method (Micromeritics ASAP 2020). The X-ray Diffraction (XRD) pattern shows that the beta-alumina was obtained with satisfactory purity.

The sample powder was compacted uniaxially, then isostatically under 60 and 250 MPa, respectively. Green compacts with relative densities of about 60% TD (Theoretical Density— 3.23 g/cm^3) were obtained. The dimensions of the compacts were 8 mm in diameter (0.5 cm^2 in area) and, approximately, 4 mm in thickness. All the current densities and electric fields mentioned in the following text were calculated using these dimensions. The compacts were characterized by XRD, Scanning Electron Microscopy (SEM)

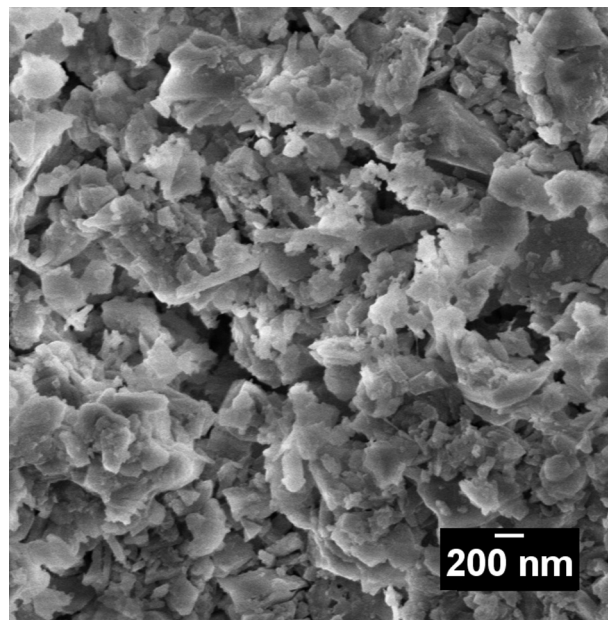


Fig. 1. SEM image of the beta-alumina green compact (pressed powder).

and Energy-dispersive X-ray spectroscopy (EDS) analysis. A SEM image of the bulk of a green compact is presented in Fig. 1. We can observe plate-shaped particles with an average size around 300 nm.

2.2. Flash sintering methodology

The experimental set-up, shown in Fig. 2, is similar to the one described in a previous paper [2]. The sample was placed in a chamber where the atmosphere can be fixed due to a gas flux (argon, hydrogen or air). The partial pressure of oxygen (PO_2) was measured by an oxygen sensor (SETNAG GEN'AIR) placed in the gas outlet. The electric field was applied through two platinum discs (10 mm in diameter and 0.5 mm thick) slightly pressed against sample's flat surfaces.

In order to improve the uniformity of the current distribution through the compact, the sample's flat surfaces were covered with

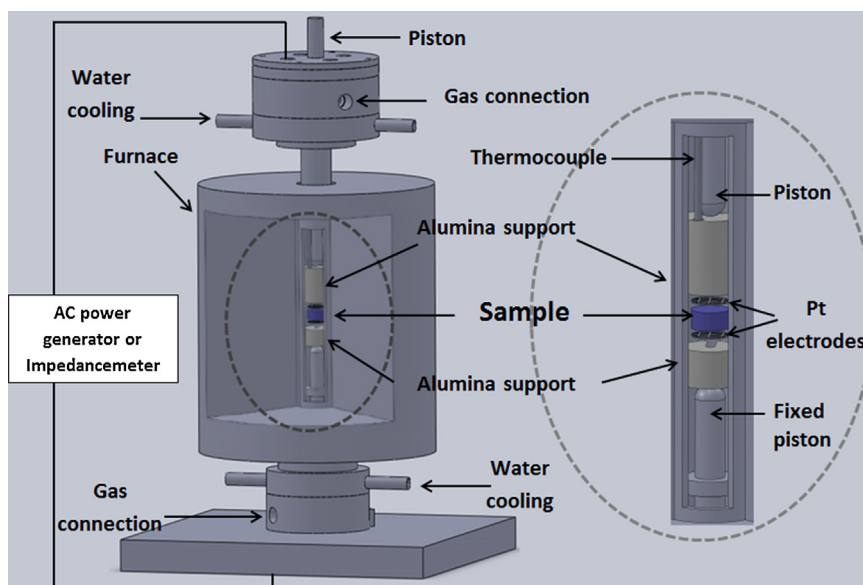


Fig. 2. Scheme of the experimental setup used for flash sintering.

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