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The effect of solids loading on the screen-printing and properties of nickel/scandia-stabilized-zirconia anodes for solid oxide fuel cells

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ABSTRACT

Screen-printing is a commonly used technique to fabricate thick film solid oxide fuel cell (SOFC) electrodes, followed by drying and high temperature sintering, and this study focuses on the rheology of such screen-printing inks for SOFC anode fabrication, and in particular on the effect of solids content. Commercially available powders of NiO and scandia stabilized zirconia were used, with average particle sizes of 0.714 and 2.151 μm, respectively. The thixotropy and viscosity of inks increased with increasing solid content. The particle network strength, important to the production of films with good particle connectivity and mechanical strength, also increased as the solids content increased. The complex modulus, G*, (indicative of the overall elasticity and tackiness of the inks) ranged from 500 to 4000 Pa, a range found acceptable for screen-printing. The minimum and maximum acceptable solids content were determined to be 25 and 30 vol% respectively. Inks having solids content outside this range were too liquid like and tacky, respectively, for effective screen-printing. The percentage of ink recovery, indicative of the print quality of the resultant films, also increased with solid content. The relevant properties of the anode films, including mechanical strength, electronic conductivity and electrochemical performance, all improved with increasing solids content as a result of improved particle connectivity, consistent with the conclusions drawn from the rheological study. In summary, from the perspective of ink rheology, screen-printability and performance, inks having 28–30 vol% solids were determined as the most suitable for the production of high quality SOFC anode films with a thickness of around 10 μm.

1. Introduction

Screen-printing is the most economical, simple and widely used technique to produce films with a thickness in the range of 10–100 μm [1–4]. There have been only a limited number of studies which seek to establish the impact of screen-printing ink on the electrode or electrolyte film properties. Hence, this study was carried out to study the relationship between ink rheology and the properties of the printed film using nickel/scandia-stabilized-zirconia (Ni/ScSZ) [5] anode inks for intermediate temperature SOFC application. The rheological properties, including viscosity, thixotropy, and viscoelasticity,

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directly influence the quality of printing and performance of the resultant films [4,6]. Viscosity and thixotropy are static properties of an ink while viscoelasticity, defined by the elastic/solid-like (G') and viscous/liquid-like (G'') moduli of the ink, represents the inks dynamic properties. Generally, a well-structured ink exhibits a large elastic modulus (indicating a high resistance towards separation and slumping) while a large viscous modulus indicates an in-elastic sample [7]. An ink with high G' value may result in ink/paste hang-up on the squeegee, limited printing speed and increased squeegee pressure, while a high G'' value may lead to increased liquid like properties and result in slumping and ink bleeding [7]. In general, the rheological properties of an ink are dependent on several factors such as the particle size and distribution of the powder [8–10], solid loading [3,10] and the composition of the ink which generally comprises a binder, a dispersant and an organic solvent [4,10,11] in addition to the powder.

As described in our previous work [4], the ingredients used in the fabrication of screen-printing inks play a critical role in adjusting the dynamic and static rheological properties of inks for the production of high quality printed films. From this work, it is clear that the particle network strength within the inks increase with increasing binder content. Additionally, the static rheological properties (e.g. thixotropy and viscosity) of the inks also increase as the binder content increases. However, the effect of solvent type on establishing a strong particle network within the inks was determined to be minimal, as confirmed by the comparable length of the linear viscoelastic region (LVR). Furthermore, the improved network strength within the inks resulted in improved particle connectivity, mechanical strength, electronic conductivity and electrochemical performance of the resultant anode films, as demonstrated in other work [12]. Other than the binder content and solvent type, the solids content is another important parameter which influences the rheology of the inks and consequently, the properties of the resultant anode films. However, this has been little studied for SOFC anode fabrication, and hence it is the impact of solids content on the rheology and properties of screen-printed SOFC anode films that is the focus of this study. As such, this paper extends our previous studies [4,12] which focussed on the effect of binder content on anode screen-printing, at a fixed solids content.

It is important to note that the maximum acceptable solids content is dependent on the particle size and distribution of the powder, in addition to the composition and type of binder and solvent type used in the ink formulation. For instance, Reid et al. [10] have produced inks using two types of yttria stabilized zirconia (YSZ) electrolyte powders having surface area of 4.31 ($d_{50} = 0.56$ μm) and 6.01 ($d_{50} = 0.37$ μm) m^2/g, respectively. In that study, the maximum acceptable solids content in the inks fabricated using the electrolyte powders with the low and high surface areas were determined to be 50 and 45 vol%, respectively. However, the viscosity of the resultant inks varied with the binder type and the specific surface area of the powders, at identical solid, solvent and binder contents in the inks. Powders with an extremely high surface area may significantly inhibit the powder content in the inks, and this may result in cracks in the resultant films due to reduced film density. It is, therefore, necessary to find the right balance between powder content and ink composition (binder, solvent and dispersant) to produce high quality films without cracks.

In addition, Von Dollen and Barnett [3] have demonstrated rheological studies on YSZ inks fabricated using three types of vehicles with different viscosity, namely A, B and C (the vehicle is a mixture of solvent and binder). The study showed that inks fabricated using vehicle C displayed the lowest viscosity followed by that fabricated using vehicles B and A, respectively. Also, the study predicted that inks having more than 40 vol% solid content were difficult to print, suggesting 40 vol% powder was the maximum acceptable. The study also demonstrated that the solvent type is another important factor in determining the maximum allowable solids content of a screen-printing ink.

In the fabrication of an electrolyte ink, a low binder content (<1 wt% of powder) [10,11] is generally used to produce dense films without defects or pinholes after binder burnout. However, in the case of electrode inks, higher binder content (>1 wt% of powder) may be preferred to improve electrode porosity after binder burnout [12,13]. The improved porosity is important to enhance the number of triple phase boundary sites of the electrode and consequently lower the electrode polarization resistance, as demonstrated in the case LSM and LSM–YSZ cathodes [13] and Ni/ScSZ anodes [12]. As a result of the high binder content in the ink formulation, the solids loading may also need to be reduced in order to control the rheology of the inks for screen-printing. Hence, the balance between solids loading and binder content is important in ink formulation to obtain inks with acceptable rheological properties and improved particle network strength. These may lead to the production of high quality films with improved particle connectivity, mechanical strength and triple phase boundary length.

The principal purpose of the present work was to study the effect of solids content on the rheological properties of NiO/10 mol%Sc_2O_3–1 mol%CeO_2–89 mol%ZrO_2 (NiO/10Sc1CeSZ) anode screen-printing ink using anhydrous terpineol, ethylene cellulose, hypermer KD15 as a solvent, binder and dispersant, respectively. These rheological studies were performed using steady-state (viscosity as a function of shear rate), dynamic (oscillation amplitude stress sweep), and creep-recovery tests. The steady-state test is used to study the thixotropic properties and viscosity of the inks while the oscillation test is generally used to characterize the visco-elastic effect of the inks represented by their elastic (G'), viscous (G'') and complex (G^*) moduli. In addition, SEM images of dried printed films were studied and correlated to the solids content. Finally, the effects of solids content on the microstructure, mechanical strength, electronic conductivity and electrochemical performance of the anode films were investigated and correlated to the rheological properties of the inks.

2. Experimental procedure

2.1. NiO/10Sc1CeSZ composite powder preparation

NiO/10 mol%Sc_2O_3–1 mol%CeO_2–89 mol%ZrO_2 (NiO/10Sc1CeSZ) composite powder, containing 40 vol% Ni and 60 vol% 10Sc1CeSZ, was prepared by mixing as-received