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The impact of ink rheology on the properties of screen-printed solid oxide fuel cell anodes

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ABSTRACT

In this study, the impact of ink rheology on the properties of screen-printed nickel/scandia-stabilized-zirconia anodes was investigated. From the rheological tests, terpineol and texanol inks with 1–3 wt% binder were suitable for screen-printing at the applied screen-printing condition, and hence these inks were used to study their rheological impact on the properties of resultant films. The mechanical hardness of anode films increased with binder content. Moreover, the electronic conductivity and electrode polarization resistance of the reduced films increased and decreased, respectively, with increasing binder content. The improved film properties can be related to the increased particle network strength within the inks, leading to improved film microstructures for application as SOFC anodes. The study also confirmed that the properties of films were more significantly affected by the binder content than solvent type, which had only a minor effect. Overall, from the perspective of ink rheology, screen-printability and performance, an ink with 3 wt% binder gave the best performance at the applied screen-printing condition.

1. Introduction

Screen-printing is widely used in the fabrication of thick film electrodes for solid oxide fuel cells (SOFCs). This technique has been extensively used in the fabrication of films of solar cells [1,2], oxides [3,4] and photoconductors [5,6]. Of greater relevance to this work, screen-printing is commonly used to produce the thick films used in solid oxide fuel cells (SOFCs), for example, thick films of yttria stabilized zirconia (YSZ) [7], gadolinia doped ceria (CGO) [8], lanthanum strontium cobaltite ferrite (LSCF) [9], lanthanum strontium magnetite (LSM) [10] and NiO/YSZ [10]. However, in all these studies, the effect of ink composition on the ink rheology was not studied and related to the performance and properties of resultant films. Furthermore, the impact of the properties of the screen-printing ink on the properties of the resultant SOFC electrode has received only limited attention to date. Hence, in this study, the rheological properties of nickel/scandia-stabilized-zirconia (Ni/ScSZ) cermet anode inks were investigated for their application in the fabrication of SOFCs. This work is an extension of our previous studies [11,12] where the correlation between ink rheology, and film properties such as quality of printed films, electrical performance and electrochemical performance, was studied as a function of the binder and solid content in the screen-printing inks.

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In general, the quality of the screen-printing process is dependent on several factors including printer settings, screen options, substrate preparation and ink rheology [7]. All these parameters can be readily controlled or adjusted during processing, other than the rheological properties of the ink. Ink rheology is characterised by measurement of viscosity or shear stress as a function of shear rate, as reported by several studies [11–16]. The rheological properties, including ink viscosity, thixotropy, and viscoelasticity, directly influence the quality of printing [11,12,15,16]. The viscoelastic property of an ink is defined by its elastic/storage and viscous/loss moduli. The elastic modulus provides information relevant to the solid-like properties, while the viscous modulus reveals the liquid-like property of the ink. These rheological properties depend on many factors such as the particle size and distribution of the powder [17,18], solid loading [7,12,13,16] and, importantly, the ingredients of the ink which generally comprise solid, binder, dispersant and organic solvent [7,11–14,16]. Generally, the processing ingredients play a critical role in controlling ink rheology, and hence in turn they would be expected to influence the properties of the resultant film.

There are many types of binders that have been used in ink formulation including polyvinylbutyral (PVB) [9,13,18,19], ethyl cellulose (EC) [11–13,16,18,19] and poly(methyl methacrylate) (PMMA) [20]. Recently, Piao et al. [19] have used EC and PVB binders (1 wt% of cermet powder) to study the microstructure of LSM cathode films. In this study, the porosity of the electrode films fabricated using EC and PVB was 30–40% and 10%, respectively. Additionally, the former showed a homogeneous pore size distribution due to its linear structure. Moreover, the LSM cathode films fabricated using EC showed a lower polarization resistance compared to films fabricated using PVB, probably due to improved porosity and particle connectivity which in turn increased the triple-phase boundary (TPB) density of the electrode film. Terpineol is a commonly used solvent to produce electrolyte paste [14,21], and in our previous work both terpineol and texanol were successfully used as solvents, in addition to ethylene cellulose as a binder, with the aim of studying the effect of both binder content and solvent type on the rheological properties of inks [11]. This earlier work showed that the effect of binder content was more significant than solvent type in establishing an effective particle network structure in the inks.

In the fabrication of an electrolyte ink, several studies have used low binder content (0.23–1.0 wt% of solid) [13,14]. This is to help ensure a dense film without defects or pinholes after volatilization of the binder during sintering [14]. However, in the fabrication of an electrode ink, a higher binder content (>1 wt%) may be preferred to improve the porosity of the electrode film, resulting from the burnout of binder during sintering [14,19]. Furthermore, a higher binder content may result in an improved particle network strength of the ink, as shown in [14] and [11]. These investigations revealed that the additional function of the binder is to improve particle connectivity, which is critical in the case of the anode ink to improve particle connectivity, and subsequently increase both the percolated triple phase boundary length and mechanical strength of the anode. On the other hand, a low binder content may cause film cracking during drying of the green film as a result of reduced particle network strength [14,18], and too high a binder content may result in poor rheology (e.g. increased tackiness) which in turn affects printability and quality [11,16]. Hence, an optimum binder content for a specific solid content should be expected. However, there have been limited studies that discuss the effect of rheology on screen-printing for solid oxide fuel cell fabrication, and in particular how this relates to the properties of the resultant film in both the green and sintered state.

In our previous work, the effect of binder content, solids loading and solvent type on the rheological properties of NiO/ 10mol%Sc_2O_3 1mol%CeO_2 - 89mol%ZrO_2 (NiO/10Sc1CeSZ) anode screen-printing inks, fabricated using texanol and terpineol solvents, has been investigated [11,12]. From the work, inks with optimum binder content and solids loading with acceptable rheological properties for the screen-printing process itself were determined. The study of solids loading has shown improved anode properties with increasing solids loading (particle connectivity, density, mechanical hardness, electrical conductivity and electrochemical performance) [12]. These improved properties are consistent with the conclusion drawn in the rheological studies in which the particle network strength within the fabricated inks increases as the solids loading increases. In the study, the binder content was fixed at 2 wt% of solids loading. However, the objective of the present work was to study the impact of the binder content and solvent type on the resultant anode properties, correlating these to the rheological properties of the inks. Nickel/scandia-stabilized-zirconia (Ni/ScSZ) anodes were selected as these show promise as anodes for intermediate temperature SOFCs [22–24]. In our study, SEM images of printed films were studied and correlated to the solvent type and binder content. Finally, the effect of binder content and solvent type on the microstructure, mechanical strength, electrical performance and electrochemical performance of the anode films were investigated and correlated to the rheological properties of the inks.

2. Experimental

2.1. *Powder preparation, ink formulation and rheological measurement*

NiO/10mol%Sc_2O_3 1mol%CeO_2 – 89mol%ZrO_2 (NiO/10Sc1CeSZ) composite powder, containing 40 vol% Ni and 60 vol% 10Sc1CeSZ, was prepared by mixing NiO powder (NexTech Materials, Ltd., USA) with 10Sc1CeSZ (NexTech Materials, Ltd., USA) powder. The BET surface areas of NiO, 10Sc1CeSZ and mechanically mixed NiO/10Sc1CeSZ powders were 3.1, 11.5 and 6.7 m^2/g, respectively. Further information on the characteristics of these powders has been presented previously [11].

The ingredients that were used in all the Ni/10Sc1CeSZ screen-printing inks are listed in Table 1. The final solids loading of the ink was 26 vol% (70 wt%) with 2.5 mg/m^2 dispersant - based on the specific surface area of the cermet powder. The amount of binder used was 0, 1, 2, 3, 4 and 5 wt% of the cermet powder respectively, and dissolved in the required solvent separately. The mixture of the ingredients was homogenized using a triple roll mill (EXAKT 80E, Germany).