Available online at www.sciencedirect.com
ScienceDirect
Ceramics International 41 (2015) 5959–5966
CERAMICS INTERNATIONAL
www.elsevier.com/locate/ceramint

Rheological analysis of ceramic pastes with ethyl cellulose for screen-printing

Koji Inukai[a,b], Yosuke Takahashi[b], Kinki Ri[c], Woosuck Shin[a,c,*]

[a]*Department of Frontier Materials, Nagoya Institute of Technology, Nagoya 466-8555, Japan*
[b]*R&D Center, Noritake Co., Ltd, Miyoshi 470-0293, Japan*
[c]*Electroceramics Processing Research Group, AIST, Nagoya 463-8560, Japan*

Received 9 December 2014; received in revised form 28 December 2014; accepted 6 January 2015
Available online 12 January 2015

Abstract

Pastes of ceramic particles are used in many industrial applications such as in printed electronic products and solid oxide fuel cells. Ethyl cellulose (EC), a polymer component in the paste, is very useful to control the rheological properties of the pastes for screen printing. In this study, to prepare ceramic $La_{0.6}Sr_{0.4}Ti_{0.3}Fe_{0.7}O_{3-\delta}$ (LSTF) pastes, EC was mixed with an organic solvent, ethylene glycol monobutyl ether acetate, and LSTF powder. The effects of EC and LSTF particle contents were investigated on the rheological properties of the pastes, using shear, stress, frequency-dependence, and a 3-step recovery tests. The recovery ratio of the pastes in the 3-step tests was found to depend strongly on their EC and LSTF particle contents, decreasing at higher contents due to the formation of a strong network. We also investigated the microstructure and surfaces of thick films fabricated through screen-printing, and confirmed that pastes with a low recovery ratio and high viscosity afford smooth surface profiles.

Keywords: Ethyl cellulose; 3-step recovery test; Recovery ratio; Screen-printing

1. Introduction

In recent years, solid oxide fuel cells (SOFCs), which can directly convert chemical energy to electrical energy, have been attracting considerable attention because of their high efficiency, low environmental impact, and fuel flexibility [1,2]. We have previously prepared $La_{1-x}Sr_xTi_{1-y}Fe_yO_{3-\delta}$ (LSTF) materials for oxygen permeable membrane reactors and obtained a high ionic conductivity for the composition $La_{0.6}Sr_{0.4}Ti_{0.3}Fe_{0.7}O_{3-\delta}$ [3,4]. This material can be used to prepare SOFC cathodes, and we have been trying to control the density and thickness of $La_{0.6}Sr_{0.4}Ti_{0.3}Fe_{0.7}O_{3-\delta}$ films using screen-printing techniques [5,6]. For industrial screen printing using ceramic pastes, a polymer—ethyl cellulose (EC) for example——is generally combined with an organic solvent [5–8,10–12]. EC is popular in industry as it affords good printing and leveling.

The rheological behavior of ceramic pastes is a topic of considerable interest for the fabrication of thick films through screen-printing. Ceramic pastes are typically non-Newtonian fluids, in other words, their viscosity is time- and shear-dependent due to the formation or breakdown of structural networks of particle-particle or particle-polymer interactions. The presence of EC modifies the rheological behavior of the pastes due to its surface affinity and ability to form hydrogen bonds [7], leading in turn to extremely complex rheological behavior. For instance, pastes containing EC have been reported to show shear thickening for nickel particles in dihydroterpineol [7] and zirconia particles in terpineol [8]. This behavior may be explained by the formation under loading shear of polymer bridges between the particles [9];

*Corresponding author at: Electroceramics Processing Research Group, AIST, Shimo-Shidami, Moriyama-ku, 463-8560, Nagoya, Japan.

http://dx.doi.org/10.1016/j.ceramint.2015.01.032
0272-8842/

this kind of effect is expected to have a crucial impact on the quality of screen-printed films.

In previous studies, we have investigated paste rheology and the interaction between EC and the particles therein, showing the relationship between the rheological behavior and the adsorption of EC on LSTF particles in organic solvent for various paste conditions [5,6]. However, during screen-printing, the complicated dynamics of the pastes is characterized by several shear rates. Screen printing pastes are designed to have a high viscosity at low shear rates to remain on the screen before the squeegee is applied. When the squeegee moves across the paste applying a high shear rate and pushing the paste through the screen mesh [12], the viscosity drops very fast [13]. Then, the viscosity of the paste is progressively recovered when the stress or shear is removed [14]. The rheological behavior of the paste immediately after shearing is key to understanding the mechanisms governing film formation through screen-printing. This can be simulated using 3-step recovery tests, which involve stepping the initially low shear rate up to high values and then back down again, with the recovery time providing a quantitative measure of the leveling and uniformity of line formation properties, as reported previously for silver paste [14]. However, the impacts of a complex rheology and a wide range of recovery properties remain unclear on the printability of ceramic pastes for thick large-area films.

In this article, we describe the rheological effects of the LSTF and EC contents of a paste prepared in diethylene glycol monobutyl ether acetate (BDGAC) solvent, using flow curve, stress sweep, frequency dependence, and 3-step recovery tests. We also investigate the microstructure and surface of screen-printed thick films.

2. Experimental method

2.1. Preparation of LSTF pastes

Powders of La_2O_3 (Wako Pure Chemical Industries, Ltd., grain size 1 μm), $SrCo_3$ (Wako, grain size 1 μm), TiO_2 (Wako, grain size 1 μm), and Fe_2O_3 (Wako, grain size 1 μm) were mixed in the necessary proportions to obtain a $La_{0.6}Sr_{0.4}Ti_{0.3}Fe_{0.7}O_{3-\delta}$ composition. The powders were mixed using a ball mill with yttria-stabilized zirconia balls for 5 h, calcined at 1200 °C for 6 h, and finally ball-milled. The average particle size (D(0.5)) of the LSTF particles was 0.93 μm and the particle size distribution was fairly uniform. The specific surface area of the powder was 4.8 m^2/g.

BDGAC (Daicel Corp., Japan) was used as a suspending medium and EC (Dow Chemical Co., USA), with an ethoxyl content of 48.0–49.5 wt%, was used as a binder.

The polymer solutions of BDGAC were prepared in a hybrid mixer (ARE310, Thinky, Japan). The polymer solution was mixed at room temperature with 60, 70, and 80 wt% LSTF powder in a roll-mill. The compositions of the different pastes prepared for this study are listed in Table 1.

Table 1
Composition of the pastes. The solvent, polymer, and oxide particles are ethylene glycol monobutyl ether acetate, ethyl cellulose, and $La_{0.6}Sr_{0.4}Ti_{0.3}Fe_{0.7}O_{3-\delta}$, respectively.

Paste	Solvent (wt%)	Polymer (wt%)	Oxide particle (wt%)
P-0–60	40.0	0.0	60.0
P-0–70	30.0	0.0	70.0
P-0–80	20.0	0.0	80.0
P-5–60	38.0 (95.0)	2.0 (5.0)	60.0 (-)
P-5–70	28.5 (95.0)	1.5 (5.0)	70.0 (-)
P-5–80	19.0 (95.0)	1.0 (5.0)	80.0 (-)
P-10–60	36.0 (90.0)	4.0 (10.0)	60.0 (-)
P-10–70	27.0 (90.0)	3.0 (10.0)	70.0 (-)
P-10–80	18.0 (90.0)	2.0 (10.0)	80.0 (-)
P-15–60	34.0 (85.0)	6.0 (15.0)	60.0 (-)
P-15–70	25.5 (85.0)	4.5 (15.0)	70.0 (-)
P-15–80	17.0 (85.0)	3.0 (15.0)	80.0 (-)

(): wt% of solvent and EC without powder.

2.2. Rheological analysis of the pastes

The flow behavior of the pastes was analyzed using a rheometer (Mars-2, HAAKE, Germany) and a parallel-plate (diameter = 35 mm) geometry. After approaching the plate to the gap, the excess paste squeezed out was wiped off. Flow curves for LSTF pastes were measured at 25 °C for shear rates increasing from 0.1 s^{-1} to 100 s^{-1} then decreasing back to 0.1 s^{-1}. In the parallel-plate setup, the gap between the plates was 0.1 mm wide. Measurements were not possible at the lowest shear rates for the samples with high particle contents because of their high viscosity; values were nonetheless recorded down to the lowest attainable shear rate.

The dynamic viscoelasticity of the pastes was quantified using the oscillation method using parallel plates (35 mm in diameter) separated by 0.1 mm. The storage modulus (G') and the loss modulus (G") were obtained using stress sweep measurements at 25 °C for shear stress values ranging from 0.1 to 1000 Pa at a frequency of 1.0 Hz. The frequency dependence of G' was measured at a stress amplitude of 10 Pa from 0.01 to 10 Hz.

To understand the rheological behavior of the pastes during screen printing, the recovery characteristics of the pastes were investigated through 3-step recovery tests, as illustrated in Fig. 1. In the first step, an oscillatory shear stress of 10 Pa was applied at 1 Hz for 60 s. In the second step, a high-rate rotational shear of 100 s^{-1} was applied to the paste for 30 s. In the third step, the initial test conditions were reapplied for 60 s. The storage modulus (G') and the loss modulus (G") were measured in the first and third steps, allowing the recovery ratio of the pastes to be calculated from the ratio of these G' values as follows:

$$\text{recovery ratio (\%)} = (G'\text{ at third step at 150 s}) / (G'\text{ at first step at 60 s}) \times 100 \quad (1)$$