Development of composite electrode materials based on nickel oxide for additive manufacturing of fuel cells

Artem Bagishev[1*], *Alexander* Titkov[1] , *Alexander* Vorobyev[1], *Tatyana* Borisenko[1], *Victor* Bessmeltsev[2], *Denis* Katasonov[2], and *Alexander* Nemudry[1]

[1]Institute of Solid State Chemistry and Mechanochemistry SB RAS, Kutateladze St. 18, Novosibirsk, 630128, Russia
[2]Institute of Automation and Electrometry SB RAS, Academician Koptyug Av. 1, Novosibirsk, 630090, Russia

Abstract. In this work, a new composition of a paste based on nanosized nickel oxide (NiO) for jet-based 3D printing has been developed and investigated. The optimal parameters of anode paste with necessary viscosity and NiO loading have been found for printing by using custom made laboratory 3D printer. Experiments have been carried out to print two- and three-dimensional test objects using the developed ceramic paste; printing modes have been investigated to fabricate objects of a given shape and size with laser sintering of the deposited layers. Experiments have been conducted for the selection of optimal temperature conditions for the post-processing of the printed samples.

1 Introduction

Alternative methods of generating electricity have received more and more attention in recent years [1]. This interest is caused, on the one hand, by a reduction in the consumption of mineral fuels, and on the other hand, by the economic efficiency of innovative approaches to power generation and strict environmental requirements for new technologies.

One of the directions of development of alternative energy is high-temperature electrochemical devices [1,2]. Such devices allow a) to efficiently (60-70% efficiency) convert fossil fuel and hydrogen into electricity by using solid oxide fuel cells (SOFCs) and b) to process carbon dioxide and water vapor into synthesis gas ($CO + 2H_2$), utilizing greenhouse emissions gases, efficiently storing energy from low-cost energy sources, using high-temperature solid oxide electrolyzers (SOE) [3]. Hydrogen is not only the basis for ecologically clean hydrogen energy, but also a raw material for various technologies of hydroprocessing, large-tonnage production of ammonia and methanol, and subsequent chemical products [4].

Structurally, SOFC can be divided into flat and tubular [1,4,5]. The planar design is widely used in stationary devices with a capacity of megawatt and above, as it provides

* Corresponding author: artembagishev15@gmail.com

good heat and mass transfer, compactness of the assembly and allows the use of standard methods of processing ceramics [6]. A significant disadvantage of the planar configuration is the high requirements for the absence of significant temperature gradients along the membrane, which can lead to the destruction of the device during thermal cycling and sharp temperature drops.

The problem can be solved by using microtubular (MT) membranes [5], the advantages of which are improved thermal and mechanical stability, ease of sealing. The rapid launch of high-temperature ECDs opens up a promising niche for compact mobile devices in transportation, military and consumer electronics applications.

A complete SOFC battery made conventional manufacturing processes usually requires many steps. All of these steps are time consuming, not easy replicable and expensive, material consuming and waste generating. Tape casting, screen printing, lamination and stacking are common procedures for making a stack of planar configuration SOFCs. In addition, a tubular SOFC stack follows the steps in which each individual cell is prepared separately and then all cells are stacked. Since there are many joints and seals in the final device, this manufacturing process greatly affects the reliability and durability of SOFC systems [1,7]. Therefore, new methods and approaches need to be developed to minimize the number of stages in the manufacture of SOFCs and, among other things, to manufacture the entire assembly at once. One of them is 3D printing, which allows fabricating complex 3D objects layer by layer from computer 3D model using a special software (CAD) [8, 9].

Freeform object manufacturing technologies such as 3D printing have only recently demonstrated their suitability for the manufacture of highly complex dense ceramic parts with good mechanical properties [10, 11]. In particular, the possibility of 3D printing of an electrolyte-supporting cell of SOFC of complex shape was demonstrated, which gave an increase in power by about 50%. [10].

In this work, we have developed and investigated the composition of paste for 3D printing. Using the prepared paste, we have successfully printed test 3D objects by custom made laboratory 3D printer and investigated its structure and morphology after printing and post processing.

2 Experimental

Nickel oxide (SOFCMAN, China), 2-Butoxyethanol (BG, Vekton, Russia), BYK (BYK-Chemie GmbH, Germany), polyvinyl butyral (PVB, Acros organics, US), dibutyl phthalate (DBF, Acros organics, US) were used to synthesize the powders.

Paste formulation and printing. The powder was preliminarily milled using an APS grinding system using bead balls (d = 1.2 mm) in ethanol. For a paste preparation BYK (loading is 8 wt% of NiO), DBF and PVB (5 wt% of BG) were dissolved in BG, placed in the APS grinding system with grinding balls (diameter 1.2 mm), then the NiO powder was added and stirred at 4000 rpm for 2 hours, then the paste was separated from the balls.

For printing, a laboratory 3D printer was used custom made by Institute of Automation and Electrometry SB RAS. The printer combines the ability to use different low and high viscous injection systems for direct jet-based printing different materials and a laser processing system based on fiber laser. The printer has a three-dimensional heated table (10x10x15 cm) for the formation of two-dimensional and three-dimensional objects. All printing experiments were performed using a pneumatic micro-metering valve and a 0.25 mm nozzle (Nordson Corporation, Germany-USA). Laser sintering of the printed layers using a fiber laser operating at a wavelength of 1.064 μm in pulse-periodic mode was performed in one pass regime with changeable laser power. The laser pulse duration and frequency were 4 ns and 250 kHz, respectively; the average power changed in the range of 0.45–2.7 W. Exposure was carried out using the raster scanning of squares 5x5, 10x10 mm^2.

The raster spacing was 0.0125 mm, the size of the focused laser beam was 0.035–0.05 mm in terms of intensity e^{-2}, and the exposure time was 0.15–0.2 ms.
Characterization. The viscosity of pastes was measured using a Brookfield DV3T-RV viscometer (Brookfield Engineering Labs Inc., USA) in cone / plate geometry at 25 ° C. A study of the samples by scanning electron microscopy (SEM) was performed using a Hitachi 3400 N scanning electron microscope (Hitachi Ltd., Japan). Microsizer 201(Microsizer, Russia) was used for the particle size distribution analysis.

3 Results and discussion

The selection of the optimal parameters of the pastes was carried out by varying the amount of polymer binder (PVB+DBF), the amount of composite powder in all pastes was constant and equal to 60 weight percent (average particle size was 1.38 μm). The viscosity of pastes depends on the amount of polymer binder in the composition, so series of pastes have been prepared with 5, 10 and 15 percent of the polymer binder. At a shear rate of 1 s^{-1}, the paste with 10% polymer binder has a viscosity of 4000 cP, and at a shear rate of 10 s^{-1} 600 cP (Fig. 1a), paste with 15% polymer binder at 1 s^{-1} has a viscosity of 25000 cP, at shear rate 10 s^{-1} - 1500 cP (Fig. 1b).

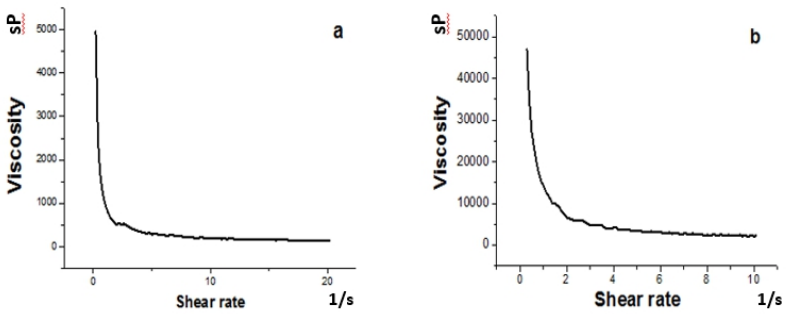

Fig.1. Viscosities of pastes at various concentrations of the polymer binder a) 10% polymer binder, b) 15% polymer binder.

To start printing 3D objects, the optimal drop was firstly selected (d_{drops} = 0.5 mm, ideal round shape after drying). For this, test printing is performed with different modes of frequency and time of opening the printhead valve. The optimal parameters for the working paste are 20Hz - valve opening frequency and 700 ms valve opening time. An array of printed dots using epy optimal parameters is presented on Fig. 2.

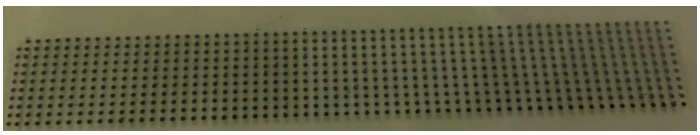

Fig.2. The array of printed dots using optimal parameters (d_{drops} = 0.5mm, ideal round shape after drying).

Next, the model of the printed object was loaded into the computer program, it was sliced into layers and the object was printed directly. Ten layers sequentially printed and subjected to a laser treatment. Laser was selectively scanned the printed pattern. The photo and SEM images of printed object are presented on the Fig. 3. Geometrical parameters of

the printed object: length - 10mm, width - 15mm, height 3mm. As can be seen on Fig. 3 b-d, the printed bar has a porous and layered structure. The grain size is about 1-2 μm. The thickness of one layer after printing is about 50 microns. Interlayer pores are closed to spherical, not connected to each other, the pore diameter varies from 5-20 microns. Most likely, the formation of porosity occurs due to the excessive pressure of gaseous products appearing during laser processing and partial decomposition of the organic components of the paste, which affect the surface of the object.

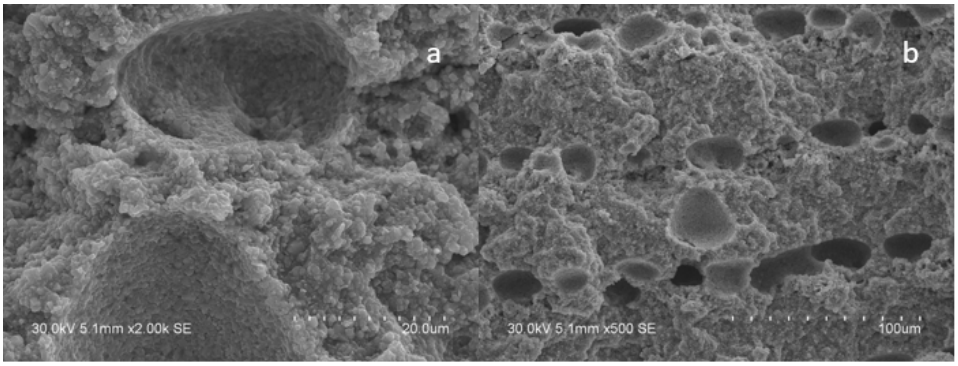

Fig.3. SEM images of the microstructure of the printed object - top view (a)-(b).

After being printed the test object was sintered in a high-temperature PVC 1.6 furnace The optimum temperature sintering for SOFC anode billets is 1400° C [12] for 11 hours in an air atmosphere, at temperatures below, the formation of a dense sintered structure of the object did not occur. Figure 4 shows a comparison of the object after sintering, in which we see that after thermal, the particles are baked together to form a dense structure. After sintering, we observe a violation of the sphericity of the pores, the coalescence of a large number of pores. During sintering, the entire object shrinks, the layered structure becomes less pronounced. Shrinkage after sintering for all geometrical dimensions was found to be around 30%.

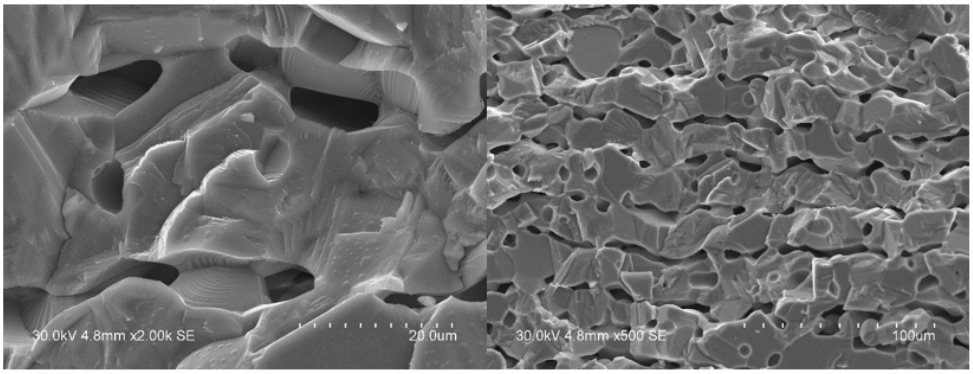

Fig.4. SEM images of the microstructure of the annealed object.

Thus, it has been shown that, using injection printing and laser processing, it is possible to form layer-by-layer 3D objects from a paste with a filler NiO. In this case, laser treatment makes it possible to partially remove the organic component and partially sinter the NiO particles together, as a result it is possible to obtain a layer-by-layer object. Using the thermal post-processing, strong sintered ceramic object can be formed with a defined 3D computer model of the shape, taking into account the shrinkage during sintering.

Further research is needed to quantify mechanical properties and their relationship to printing conditions.

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