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Processing of manganite-based contact layers for stacking of planar solid oxide fuel cells

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Abstract:	Assembling of planar solid oxide fuel cell (SOFC) stacks makes it necessary to form stable, highly conductive contact layers between the stainless-steel current collectors and ceramic cathodes. In this work, mechanical pre-treatment conditions of submicron $La_{0.8}Sr_{0.2}MnO_{3\pm\delta}$ (LSM) powders were optimized in order to sinter mechanically stable contacts in the course of SOFC sealing procedure without use of inorganic sintering aids. Excessive ball-milling time and/or rotating speed was shown to result in partial decomposition of the perovskite phase, which increases electrical resistivity of the porous layers. Testing of the LSM contact layers in model SOFC stack with Crofer 22H current collectors demonstrated sufficient adhesion and performance.
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	Vladimir A. Sobyanin, DrS head of the laboratoty, Boreskov Institute of Catalysis SB RAS: FGBUN Institut kataliza im G K Boreskova Sibirskogo otdelenia Rossijskoj akademii nauk sobyanin@catalysis.ru Professor Sobyanin is famous for his works in a field of fuel processors for fuel cell applications
	Mikhail V. Patrakeev, DrS leading researcher, Institute of Solid State Chemistry of the Ural Branch of the Russian Academy of Sciences: FGBUN Institut himii tverdogo tela Ural'skogo otdelenia Rossijskoj akademii nauk patrakeev@ihim.uran.ru Dr. Patrakeev is an author of numerous works in a direction of new materials of SOFC application.

Dear Editor,

Please find attached for your kind review our manuscript entitled “Processing of manganite-based contact layers for stacking of planar solid oxide fuel cells”. Work was done by E.A.Agarkova, D.V.Matveev, Yu.S.Fedotov, A.I.Ivanov, D.A.Agarkov, S.I.Bredikhin, at the Institute of Solid State Physics RAS, Moscow Institute of Physics and Technology.

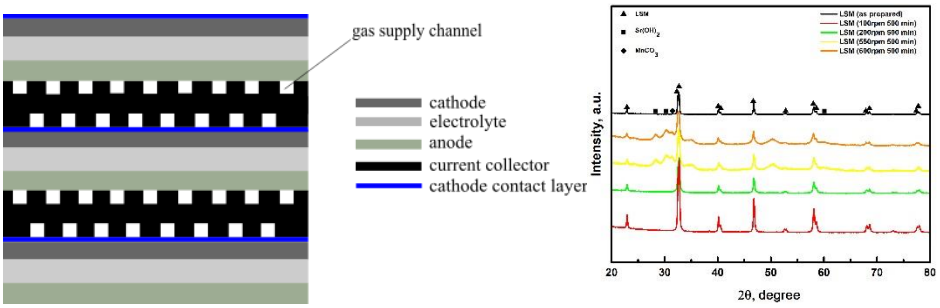
In this work, cathode electrode and current collector $La_{0.8}Sr_{0.2}MnO_{3\pm\delta}$ (LSM) powder was synthesized via glycine-nitrate method in order to obtain good adhesion and electrical contact between solid oxide fuel cells (SOFCs) and current collectors made of ferritic stainless steel. Grinding at speeds of 100, 200, 550 and 600 rpm during 300-500 minutes in stabilized zirconia balls was used in order to improve electrochemical performance of the layer prepared basing on synthesized powder. Increase in grinding speed leads to LSM decay on $Sr(OH)_2$ and $MnCO_3$. In turn, ball milling at 200 rpm during 500 minutes leads to the decrease in average grain size and, as a consequence, to the enhancement of the electrochemical characteristics. Look forward to your favorable consideration.

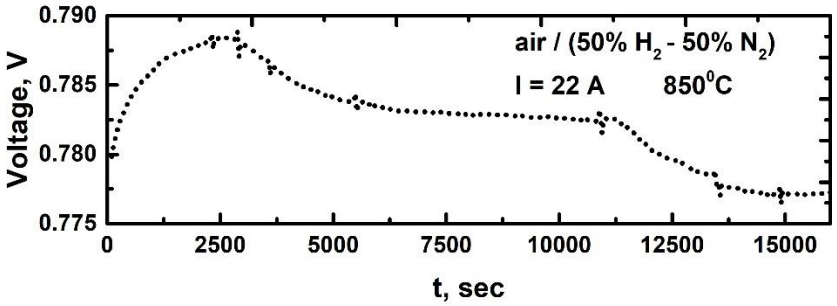
Yours sincerely,

Dmitrii Agarkov,

Moscow Institute of Physics and Technology

Graphical Abstract





- LSM powder was synthesized by glycine-nitrate method
- Grinding treatment enhance LSM electrochemical performance

Processing of manganite-based contact layers for stacking of planar solid oxide fuel cells

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Abstract

Assembling of planar solid oxide fuel cell (SOFC) stacks makes it necessary to form stable, highly conductive contact layers between the stainless-steel current collectors and ceramic cathodes. In this work, mechanical pre-treatment conditions of submicron $La_{0.8}Sr_{0.2}MnO_{3\pm\delta}$ (LSM) powders were optimized in order to sinter mechanically stable contacts in the course of SOFC sealing procedure without use of inorganic sintering aids. Excessive ball-milling time and/or rotating speed was shown to result in partial decomposition of the perovskite phase, which increases electrical resistivity of the porous layers. Testing of the LSM contact layers in model SOFC stack with Crofer 22H current collectors demonstrated sufficient adhesion and performance.

Keywords: planar SOFC, contact materials, current collection, LSM, stability.

1. Introduction

Electric power plants based on solid oxide fuel cells (SOFCs) provide environmentally friendly co-generation of the electricity and high-potential heat with minimum emissions [1,2]. Conventional planar SOFC stacks consist of alternating membrane-electrode assemblies (MEA) and ferritic stainless steel current collectors with the gas flow channels [3-5]. In turn, MEAs are the multilayered ceramic plates comprising a gas-tight solid electrolyte membrane and porous anode and cathode; each functional MEA layer may also consist of several sublayers [4,6]. This architecture is illustrated in Fig.1.

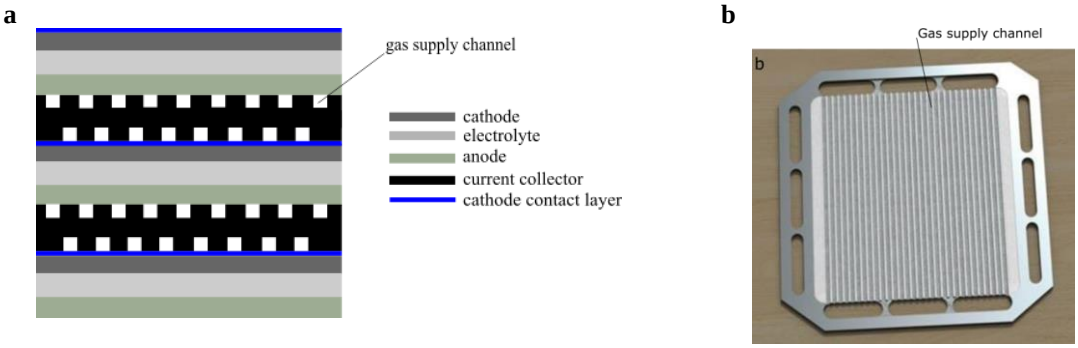


Fig.1. Schematic drawing of the planar SOFC stack architecture (a) and photo of the Crofer-22H stainless-steel bipolar plate with the gas supply channels (b).

The interfaces between both electrodes and current collectors should have a low electrical resistivity and a sufficient stability in order to provide stack lifetimes of, at least, 30-50 thousands of hours [7,8]. At the anode side, good adhesion and electrical contact can be achieved by the application of metallic meshes [8]. The conditions inside the SOFC cathode chamber, primarily oxidizing atmosphere at elevated temperatures and high current densities, are more corrosive for metals such as stainless steel and nickel. This factor makes it necessary to apply non-metallic conductive layer at the cathode | current collector interface [9-11]. The present work was centered on processing of the contact layers made of lanthanum-strontium manganite (LSM), the conventional SOFC cathode component, without sintering aids and their testing for SOFC stacking.

2. Experimental section

Single-phase submicron powder of perovskite-type $La_{0.8}Sr_{0.2}MnO_{3\pm\delta}$ (LSM) was synthesized by the glycine-nitrate technique using high-purity $La(NO_3)_3\ 6H_2O$, $Sr(NO_3)_2$ and $Mn(CH_3COO)_2\ 4H_2O$ as starting materials [12]. The pre-final thermal treatment of the powder was carried out at 750°C in air.

As-prepared LSM was ball-milled in ethanol using yttria-stabilized zirconia (YSZ) balls and planetary-type Pulverisette 6 instrument (Fritsch). Milling was performed for 300 and 500 minutes varying the rotation speed from 100 up to 600 rpm. Then LSM powder was dried and mixed with binder (9 wt.% polyvinyl butyral - PVB, Butvar B-98, supplied by Acros Organics, USA), plasticizer (2 wt.% diethyl adipate, Merck), dispersant (2 wt.% diamine RRT, UPI Chem, USA), and solvent (70:30 vol.% mixture of

toluene and butanol). The slurry was homogenized in a Thinky ARE-250 planetary mixer at a rotation speed of 600 rpm during 30 minutes.

Phase composition of the powders was studied by X-ray diffraction (XRD, Siemens D-500, $CuK_{\alpha 1}$ radiation). The powder morphology was characterized by the transmission electron microscopy (TEM, JEOL JEM-100CX). Microstructure of the contact layers prior to and after operation was assessed by the scanning electron microscopy (SEM, Supra 50 VP, Carl Zeiss). Thermogravimetric analysis (TGA) was performed using a Setaram Setsys Evolution 16/18 instrument in flowing air. Electrical resistivity of the LSM layers, similar to those tested in the SOFC stack and deposited onto YSZ ceramics under identical conditions, was measured by the 4-probe method at 600-950°C on heating and subsequent cooling in air.

Performance of the manganite contact pastes was tested using a single SOFC unit sandwiched between two stainless-steel current collectors. The collectors shown in Fig.1(b) were made of the Crofer 22H steel (ThyssenKrupp) with subsequent electrodeposition of protective Ni layers. The three-layer solid electrolyte membranes 6ScSZ/10Sc1YSZ/6ScSZ (6ScSZ: 6 mol.% Sc_2O_3 stabilized ZrO_2; 10Sc1YSZ: 10 mol.% Sc_2O_3 and 1 mol.% Y_2O_3 co-stabilized ZrO_2) with the thickness of 150 μm and area of 10x10 cm^2 were produced by NEVZ-Ceramics (Russia). The anode comprised four layers, including $Ce_{0.8}Gd_{0.2}O_{2-\delta}$ (GDC) deposited directly onto the zirconia membrane, electrochemically active functional layer of NiO/GDC composite (50:50 wt.%), current-collecting layer of NiO/10Sc1CeSZ composite (60:40 wt.%; 10Sc1YSZ: 10 mol.% Sc_2O_3 and 1 mol.% CeO_2 co-stabilized ZrO_2), and the contact NiO layer. The cathode consisted of three layers made of GDC deposited onto the electrolyte, LSM/GDC (60:40 wt.%) composite, and single-phase LSM. The multilayered electrodes were deposited by screen-printing [4, 6] and then co-sintered at 1250°C. The contact LSM paste was applied onto the sintered cathode. Following final assembling of the MEA, two current collectors and Ni mesh into the model stack, sealing was performed under the mechanical load of 0.4 kg/cm^2 at 940°C. The electrochemical measurements were carried out using a Reference 3000 potentiostat (Gamry, USA) equipped with an additional Reference 30K Booster module. The tests were performed at 850 °C with 50% H_2 - 50% N_2 mixture as fuel and atmospheric air as oxidant.

3. Results and discussion

Selected results of XRD analysis and the average particle sizes, extracted by statistical treatment of the TEM and SEM data for as-synthesized and grinded LSM powders, are presented in Table 1 and Fig.2(a). Briefly, grinding at 550 and 600 rpm led to partial LSM decomposition and an appearance of $Sr(OH)_2$ and $MnCO_3$ phases. The minimum grain size of single-phase powders was achieved after grinding at 200 rpm during 500 minutes. The LSM powder used to prepare contact paste was, therefore, ball-milled in these conditions.

Table 1. Results of XRD analysis and average particle sizes of as-synthesized and grinded powders

Rotation speed (rpm) / grinding time (min)	Particle size		Single phase preservation
	Agglomerates (SEM), μm	Grains (TEM), nm	
As-synthesized	5.8	110	+
100/300	18	65	+
100/500	12	31	+
200/300	20.4	58	+
200/500	3.6	42	+
550/300	6.2	33	−
550/500	13.6	27	−
600/300	2	30	−
600/500	2.4	33	−

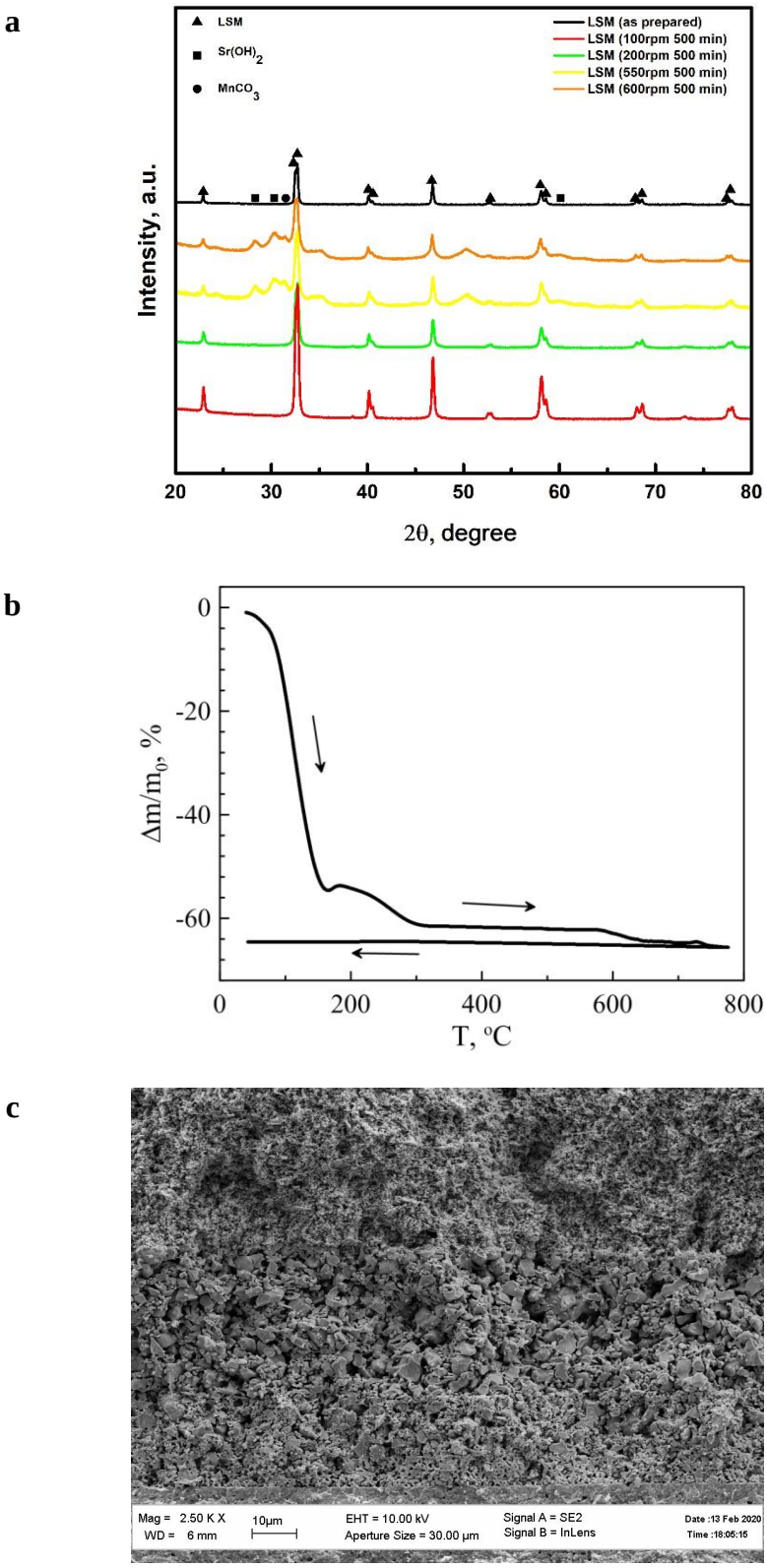
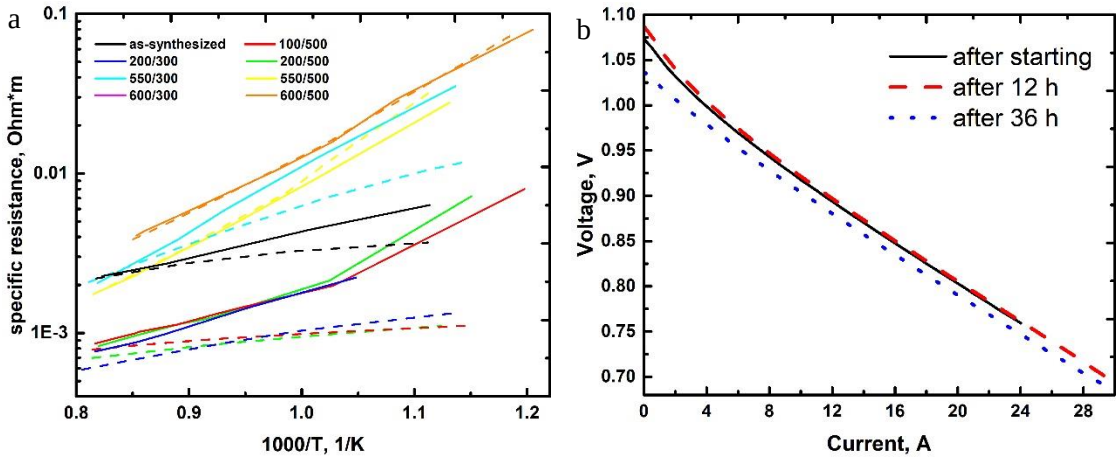


Fig.2. XRD patterns of as-synthesized and grinded LSM powders (a), TGA curves of the manganite paste on heating and cooling in air, and typical microstructure of the LSM contact layer after SOFC tests (c).

Thermogravimetric analysis of the LSM paste showed that the weight of remaining manganite becomes constant on heating above at 700-750 °C (Fig.2b). This ensures that all organic additives are completely removed prior to SOFC sealing at 940 °C. At the same time, the contact layer sintered in the course of SOFC sealing, remains sufficiently porous to provide an absence of gas diffusion limitations (Fig.2c).

The results of electrical resistivity tests of the sintered LSM layers are presented at Fig.3(a). The contact layers made of the powders pre-activated by grinding exhibit a higher conductivity in comparison with the layer made of as-synthesized LSM. At the SOFC operating temperatures, the difference between the corresponding values is up to approximately 3 times. In the cases when increasing ball-milling speed and/or time leads to partial decomposition of the perovskite phase, the electrical resistance becomes higher.

The current-voltage dependencies of the model SOFC after sealing and after 12 and 36 h testing under steady-state conditions are presented in Fig.3(b). Fig. 3(c) displays time dependence of the voltage under fixed current density. In general, the use of LSM contact layer made it possible to achieve sufficiently high currents and a stable operation. Although a minor decrease in the SOFC performance was observed after 36 h, this phenomenon is clearly associated with decreasing open-circuit voltage under zero current (Fig.2a), which suggest an appearance of small gas leakages. Microstructural analysis of the LSM contact later after SOFC tests did not reveal any significant defects like cracks or exfoliation (Fig.2c).



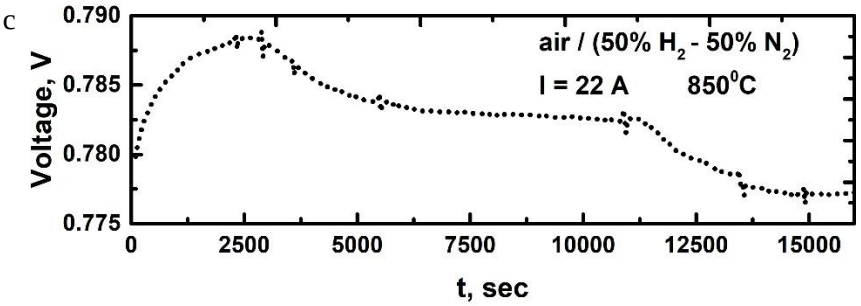


Fig.3. Specific electrical resistivity of the contact layers made of various LSM powders (a), current-voltage curves (b) and voltage vs. time dependence of the model SOFC assembled with the LSM contact layer under 22A current load (c). The solid and dashed lines in (a) correspond to the data collected on initial heating and subsequent cooling, respectively.

4. Conclusions

Submicron LSM powder was synthesized by the glycine-nitrate technique as a precursor for contact layers between the SOFC cathodes and ferritic stainless steel current collectors. Pre-grinding treatment conditions were optimized in order to decrease grain size, to increase electrical conductivity and to enable formation of mechanically stable contact layers without use of inorganic sintering aids. Ball-milling at 200 rpm during 500 minutes makes it possible to achieve these goals. Excessive rotating speeds and/or time was found to result in partial decomposition of the LSM perovskite phase, leading to worse electrical properties. Successful use of the LSM contact material without inorganic additives was demonstrated in model planar SOFC unit with the geometric area of 10x10 cm^2.

Acknowledgments

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Figure

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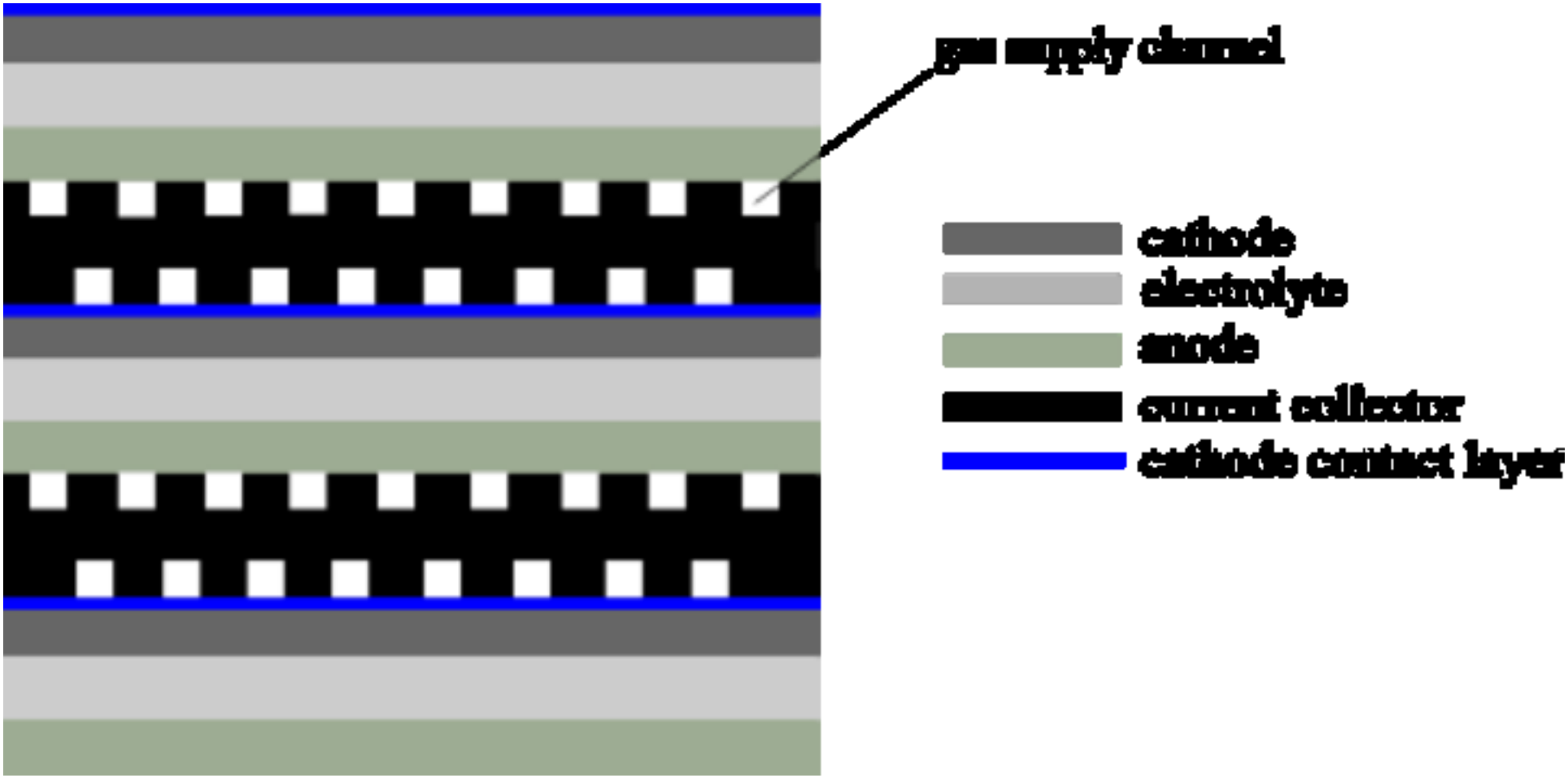

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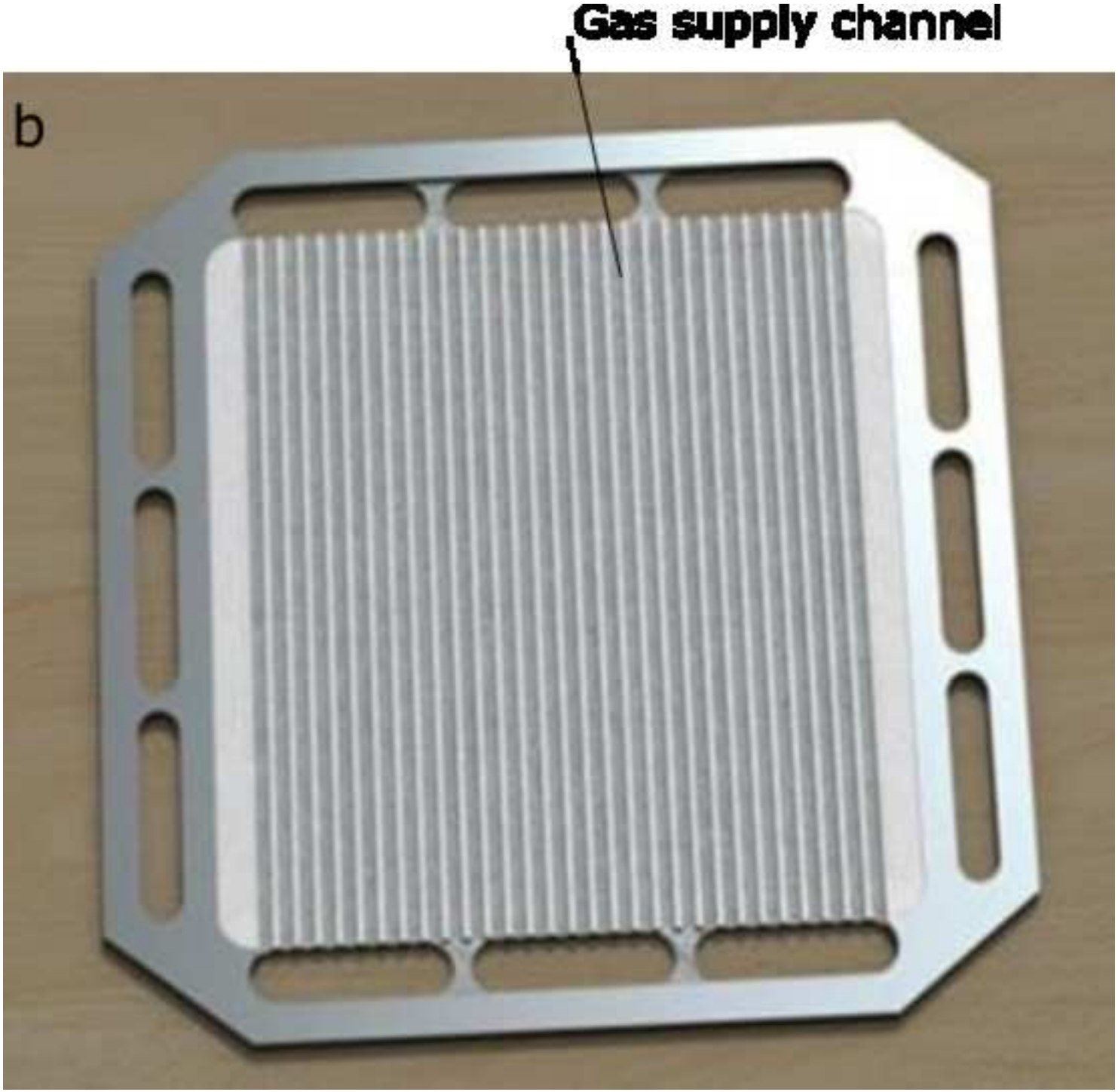

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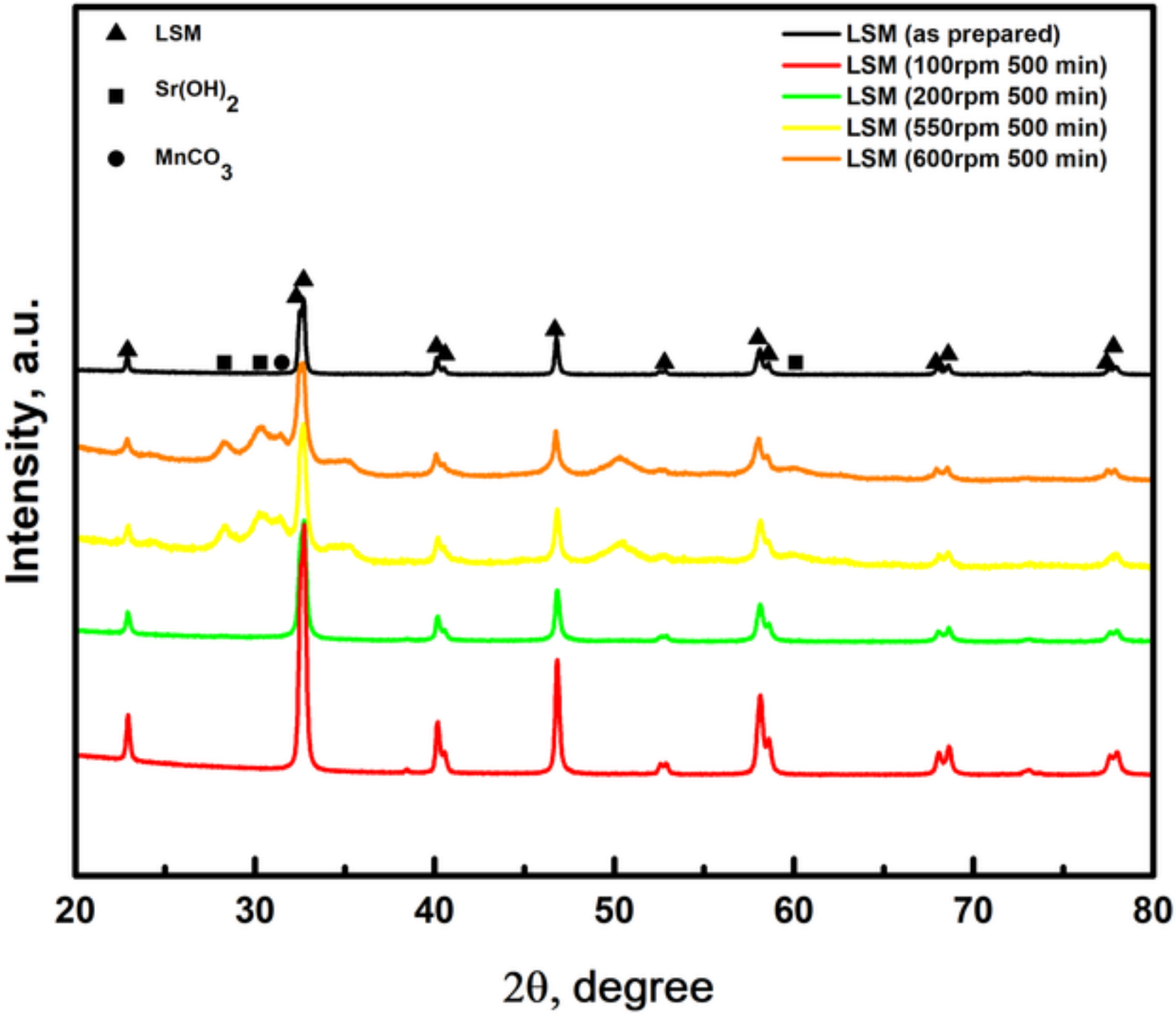

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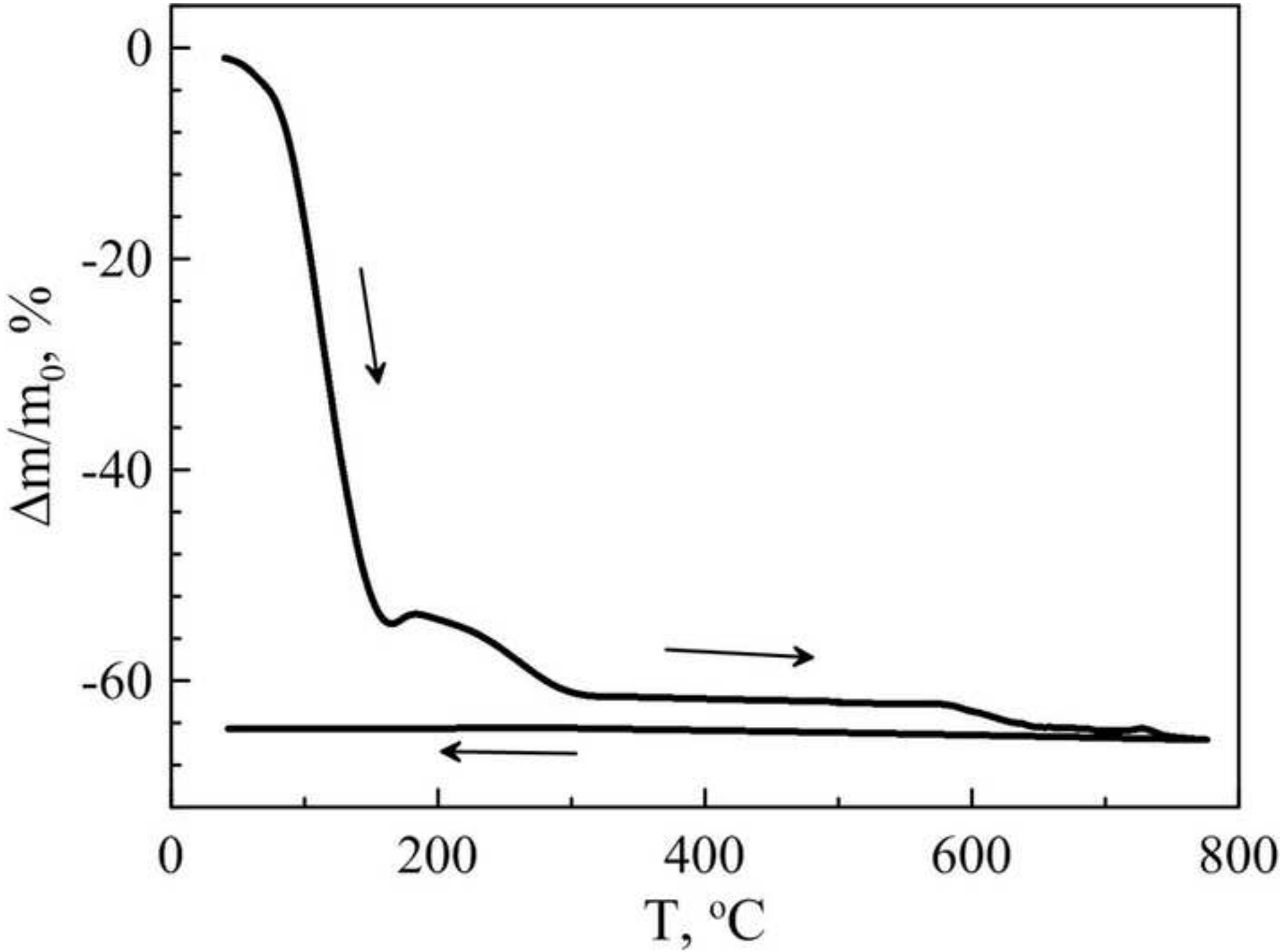

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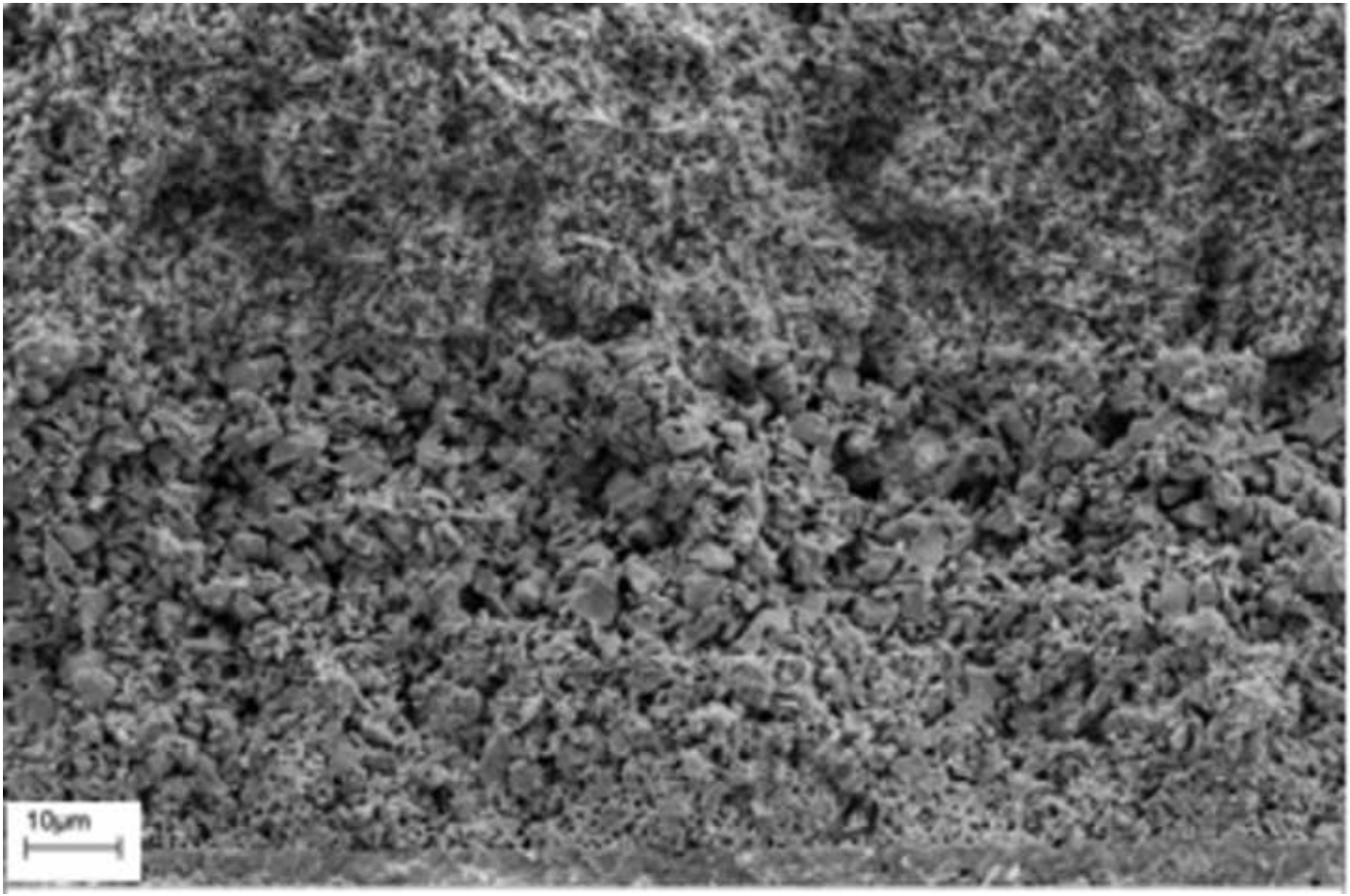

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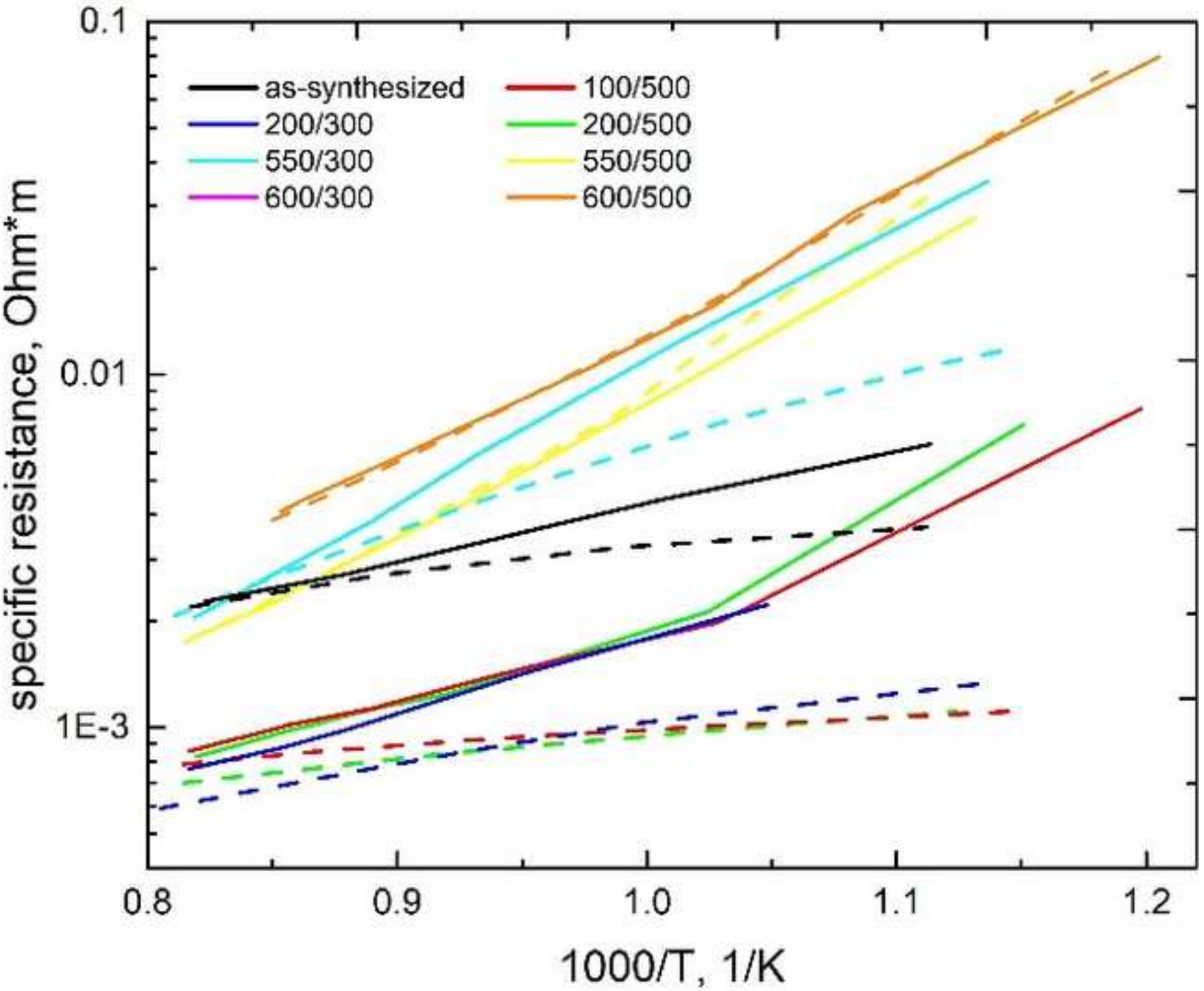

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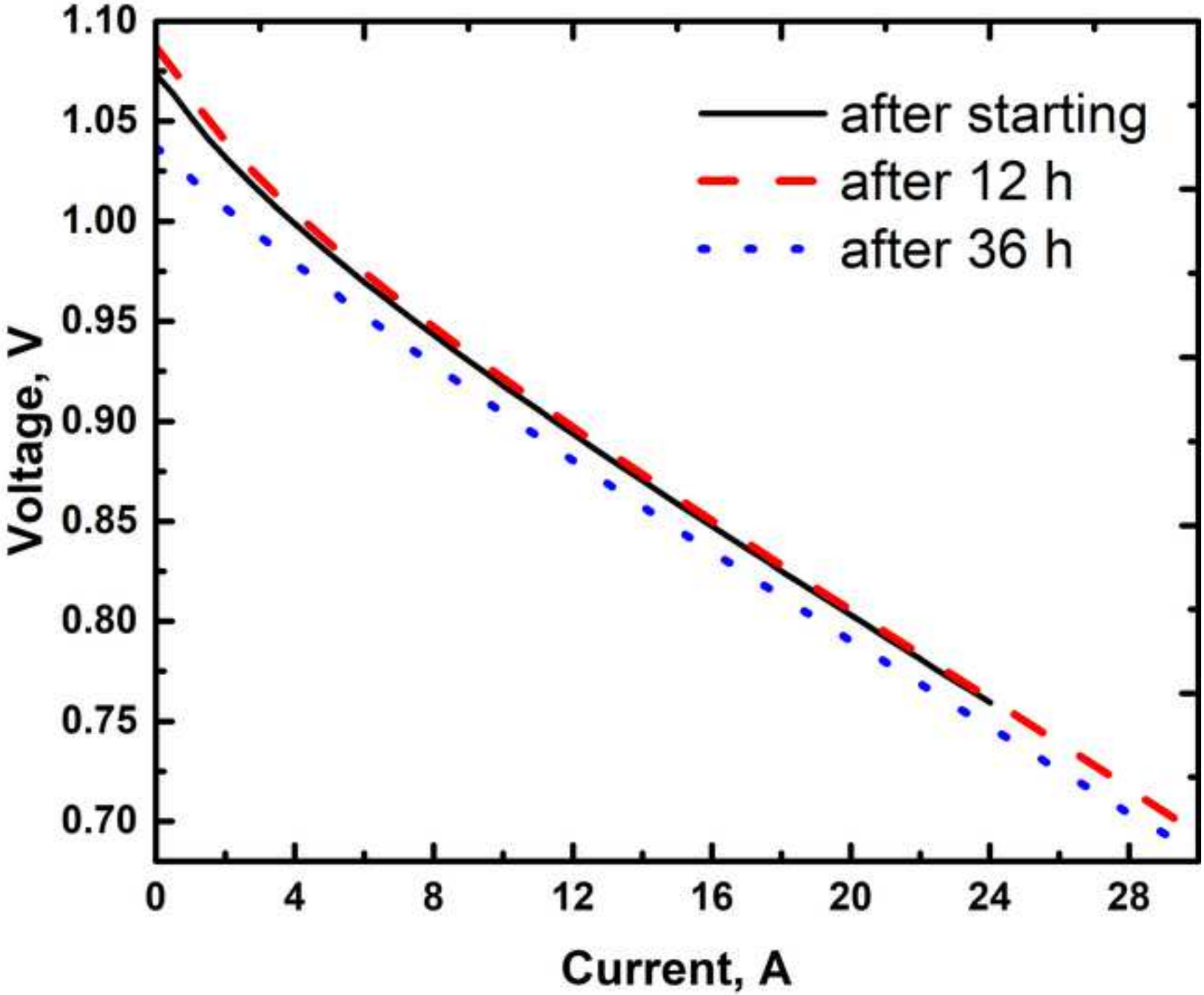

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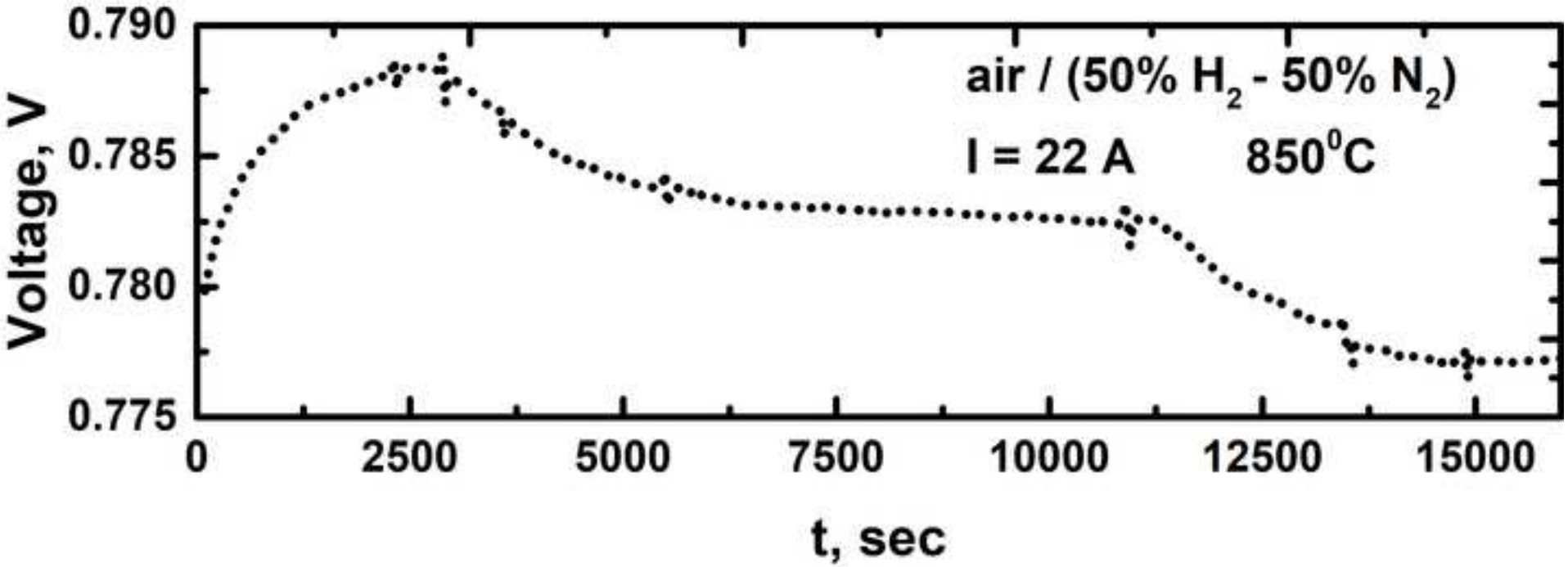

Table

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E.A.Agarkova – Data curation, Investigation, Writing – original draft

D.V.Matveev – Data curation, Investigation

Yu.S.Fedotov – Data curation, Investigation

A.I.Ivanov – Data curation, Investigation

D.A.Agarkov – Writing – original draft, Writing – review & editing

S.I.Bredikhin – Supervision, Methodology

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