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## COMPOSITE Ag-La<sub>0.8</sub>Sr<sub>0.2</sub>MnO<sub>3-σ</sub> CATHODE FOR SOLID OXIDE FUEL CELLS

### KOMPOZYTOWA KATODA Ag-La<sub>0.8</sub>Sr<sub>0.2</sub>MnO<sub>3-σ</sub> DLA STAŁOTLENKOWYCH OGNIW PALIWOWYCH

Composite cathodes for solid oxide fuel cells composed of metallic silver dispersed in ceramic (La<sub>0.8</sub>Sr<sub>0.2</sub>MnO<sub>3-σ</sub>) matrix were prepared on the surface of solid electrolyte by two-step procedure. First the matrix of controlled porosity was created by sintering mixture of La<sub>0.8</sub>Sr<sub>0.2</sub>MnO<sub>3-σ</sub> powder with the organic polymer beads then the matrix was saturated with AgNO<sub>3</sub> solution and sintered again. Such obtained cathodes showed higher electrical conductivity and lower charge transfer resistance in oxygen reduction reaction in comparison to pure ceramic cathodes.

*Keywords:* Intermediate-temperature solid oxide fuel cells; Silver-LSM composite cathode, oxygen reduction reaction

Na powierzchni elektrolitu stałego wytwarzano kompozytowe katody dla stałotlenkowych ogniw paliwowych zbudowane z metalicznego srebra rozproszonego w osnowie z La<sub>0.8</sub>Sr<sub>0.2</sub>MnO<sub>3-σ</sub>. Osnowę o kontrolowanej porowatości otrzymywano przez prażenie mieszaniny proszku La<sub>0.8</sub>Sr<sub>0.2</sub>MnO<sub>3-σ</sub> z kulkami z tworzywa organicznego. Porowatą osnowę nasycano roztworem AgNO<sub>3</sub> i ponownie wyprażano. Tak otrzymane katody wykazywały wyższą przewodność elektryczną i niższą oporność aktywną w reakcji redukcji tlenu w porównaniu z katodami z czystej ceramiki.

### 1. Introduction

Designing materials for solid oxide fuel cells (SOFCs) working at the high temperatures presents a challenge for material engineering. So, it is not surprising that the research in the field of SOFCs concentrates nowadays on reducing the working temperature to the intermediate temperature (IT) range (500-700°C). One of the main problems in the development of IT SOFCs is the slow reduction of oxygen at the cathode. Lowering temperature opens new horizons because some cathode materials that cannot be applied at the high temperatures can be reconsidered now for the use in IT range. One of such materials is metallic silver. Silver is the best electronic conductor, it is ductile and cheap, exhibits excellent electrocatalytic properties for the oxygen reduction reaction (ORR) [1] but cannot be used at high temperatures due to its low melting temperature (961°C), high volatility and susceptibility to migration in the electric field [2-6]. Lanthanum strontium manganite La<sub>0.8</sub>Sr<sub>0.2</sub>MnO<sub>3-σ</sub> (LSM) is the state of the art SOFC cathode material. Several attempts to improve the performance of the LSM cathode by the addition of silver were described [7-10]. Composite cathodes made of LSM and Ag cannot be prepared simply by sintering LSM with Ag because preparation of LSM cathode requires sintering at the temperature of 1100°C. Shoklapper et al. [7] prepared Ag-LSM cathodes by saturation of LSC cathode with AgNO<sub>3</sub>

solution then conditioning upon polarization, achieving evenly dispersed silver layer and 50% rise of cell power. Haanappel et al. [8] obtained Ag-LSM composite cathodes by four routes but they did not achieve a considerable progress in the performance after the silver addition. Uhlenbruck et al. [9] obtained Ag-LSM composite cathodes containing 0.1-2% silver by the addition of silver nitrate to the initial mixture of metal nitrates during synthesis of LSM. They showed that performance of electrode increases with the increase of silver content. Wang et al. [10] synthesized Ag-LSM powder then made cathodes by the screen printing method and sintering again at 850°C. They achieved the decrease of electrode impedance as compared to pure LSM electrodes obtained in the similar way. Cathode in an SOFC should show high porosity and good electrical conductivity. In our work the composite cathodes Ag-LSM of high and controlled porosity were prepared on the surface of solid electrolyte Sm<sub>0.2</sub>Ce<sub>0.8</sub>O<sub>1.9</sub> (samarium doped ceria – SDC) by two-step procedure. First the matrix of controlled porosity was created by sintering La<sub>0.8</sub>Sr<sub>0.2</sub>MnO<sub>3-σ</sub> powder with the organic polymer beads then the matrix was saturated with AgNO<sub>3</sub> solution and sintered again. The performance of cathodes was checked by measuring the kinetic of the ORR at the solid electrolyte/cathode interface by electrochemical impedance spectroscopy (EIS).

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## 2. Experimental

The silver (99.99%) and platinum (99.98%) wires (both 0.5 mm in diameter) were supplied by Mennica Polska S.A, Poland. The SDC pellets were formed from SDC powder (Terio Inc., Qingdao, China) and distilled water, isostatically pressed at the pressure of 62 MPa and sintered at 1660°C for 2 hours, then polished. The samples were shaped to the form of discs of 20 mm in diameter and thickness of 0.8 mm. LSM (Ningbo Institute of Materials Technology and Engineering, Ningbo, China), was ball milled in a rotary-vibratory mill (Pulverisette 6, Fritsch, Germany) for 48 hours in dry ethyl alcohol using zirconia grinding media to obtain particles of the diameter 0.2-0.6  $\mu\text{m}$ . Suspension of LSM particles in ethyl alcohol was mixed with the suspension in ethyl alcohol of functionalized polystyrene microspheres of the diameter 2.5  $\mu\text{m}$  (Polysciences Inc, USA) in the proportions: 1g of LSM and 0.5g of polystyrene beads in 20 ml of ethyl alcohol. The alcohol suspensions were homogenized for five minutes using ultrasonic homogenizer (Vibra Cell, Sonics and Materials Inc, USA) at a frequency of 40 kHz. The suspension was then dropped on the surface of the electrolyte pellet, dried and calcined during two hours at the temperature of 1200°C. To prepare the Ag-LSM composite cathode the porous LSM layer was saturated with the 0.05 mol  $\text{dm}^{-3}$   $\text{AgNO}_3$  solution containing also ethylene glycol (7 mol  $\text{dm}^{-3}$ ) and citric acid (3.25 mol  $\text{dm}^{-3}$ ). The electrolyte pellet with the deposited LSM cathode saturated with silver salt solution was dried and sintered during two hours at 600°C. The cathode layer was divided in two parts, by making sharp scratch across the surface. Part of the cathode layer served later as a working electrode, the other part as a reference electrode. The Mn/Ag proportion in such prepared electrode was 70:1 (analyzed using EDX3600H Alloy Analyzer, Skyray Instruments, USA). In all cases of sintering the temperature of the oven was raised from the room temperature to the temperature of sintering at the rate of 2°C  $\text{min}^{-1}$ . Other chemicals used were of the analytical reagent grade purity. The phase composition of all powders and sintered samples was identified by X-ray diffraction (XRD) analysis basing on the ICDD data base. XRD measurements were performed using the Panalytical X'Pert Pro system with monochromatic Cu  $K_\alpha$  radiation. The microstructure observations were carried out by means of the scanning electron microscope (SEM) JEOL JSM-7500F with INCA PentaFetx3 EDS system. Impedance spectra were measured using Gamry 300 series potentiostat/galvanostat/ZRA (Gamry Instruments, USA) in the three electrode setup at the rest potential of the Ag-LSM electrode in the frequency range 0.1 to 300000 Hz and with the amplitude of the sinusoidal voltage signal 5 mV. The counter electrode was a flat coil made of silver wire pressed to the rear side of the electrolyte. More details about the measuring setup and the measuring procedure may be found in our earlier papers [4-6]. The EIS measurements were performed at the temperatures 600 and 700°C at different concentrations of oxygen in argon-oxygen mixtures at the atmospheric pressure.

## 3. Results

Fig. 1 presents the SEM microphotographs of the LSM cathode before the introduction of silver. Both particular LSM grains as well as holes of the diameter  $\sim 2.5 \mu\text{m}$  are clearly visible. There are also cracks on the surface of the cathode, so it may be stated that the prepared LSM cathode shows high and diverse porosity and good conditions for  $\text{AgNO}_3$  solution to infiltrate into the cathode body.

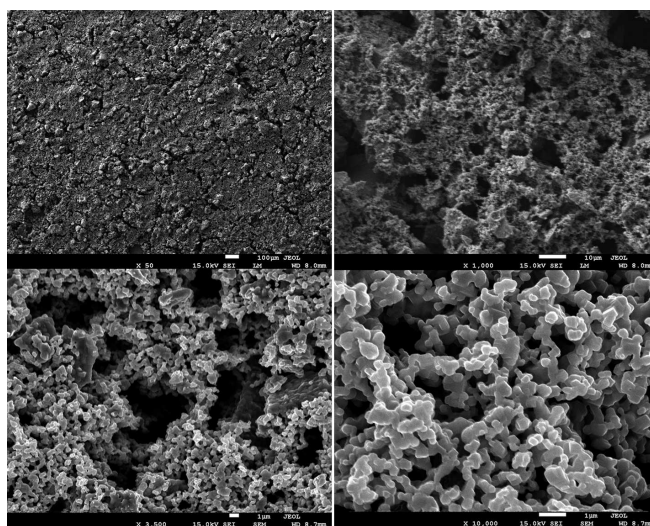


Fig. 1. SEM pictures at the different magnifications of the LSM cathode after sintering but before the introduction of silver, view from the top

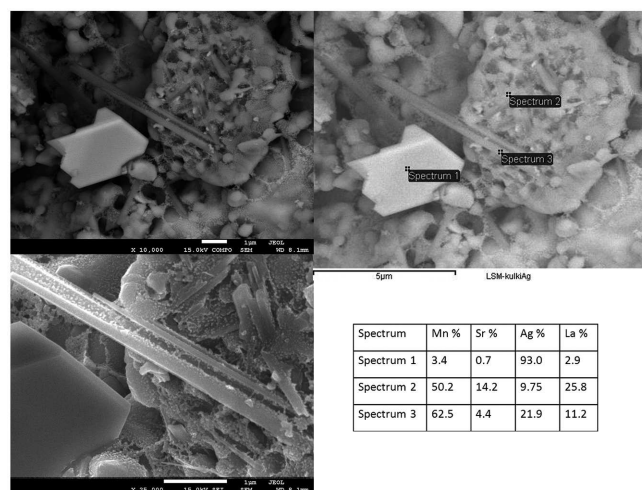


Fig. 2. SEM pictures at two different magnifications of the LSM cathode after introduction of silver and sintering, view from the top (left), and the picture in the reflected electron mode of the same area (right). In that mode the brightness of the picture is proportional to the atomic number of the element and the density of the material. Results of the EDS analysis performed at the particular points are also given in the picture in the form of a table

Fig. 2 presents the SEM microphotographs of the cathode after the saturation with the  $\text{AgNO}_3$  solution and sintering and Fig. 3 the same cathode after 10 days of experiments. Every day a cycle of EIS measurements was performed, between measurements the cathode was kept at the temperature

of 600°C. Three types of silver structures are seen in the composite: big crystals (of the diameter roughly equal to or lower than 2.5  $\mu\text{m}$ ), silver needles of the diameter from few tenths to few hundredths nanometers and the length of up to about 10  $\mu\text{m}$  and fine silver nanocrystals of the diameter below 0.1  $\mu\text{m}$  decorating the LSM grains (better visible in Fig. 3, right). Much more needles and nanocrystals was observed in the cathode after the reaction cycle than before (compare Fig. 2 and Fig. 3). The chemical identity of the observed objects was confirmed by EDS analysis (see the table in Fig. 2).

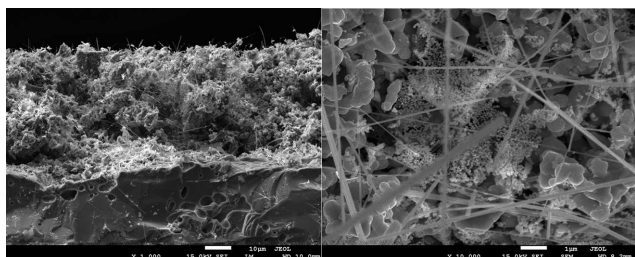


Fig. 3. SEM pictures of the section of the system electrolyte-cathode (left) and the cathode viewed from the top (right) after 10 days (see the text for the explanations). Note the fine Ag crystals decorating the LSM grains

Data from the table in Fig. 2 suggest increased concentration of manganese around the silver needle. Although the electron beam spot in EDS (1.5  $\mu\text{m}$ ) was much wider than the needle diameter, it was possible to confirm that making the EDS analysis along the line perpendicular to the long axis of the needle. As can be seen from Fig. 4 when the electron spot crosses the needle, the increase in the concentration of silver is accompanied by the decrease in the concentration of lanthanum, whereas the concentration of manganese seems to increase. That aspect of the composite electrode preparation is being now investigated in our laboratory.

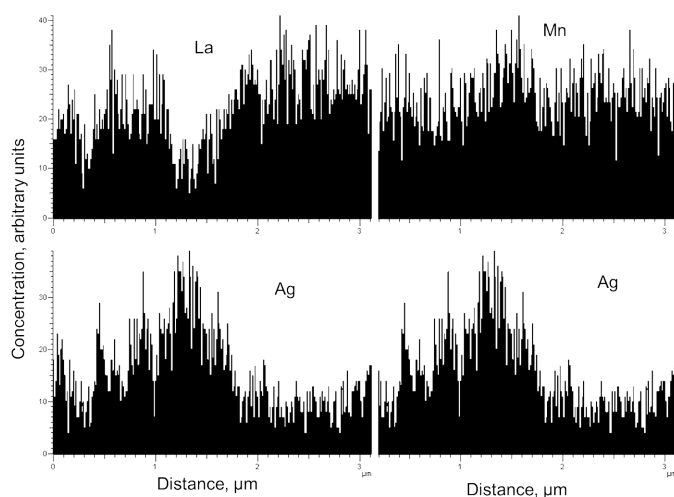


Fig. 4. EDS analysis of the cathode material composition along the line perpendicular to the long axis of the silver needle visible in Fig.3

Except diffraction lines belonging to LSM ( $\text{Sr}_{0.3}\text{La}_{0.7}\text{MnO}_3$  according to the database) and SDC ( $\text{Sm}_{0.1}\text{Ce}_{0.9}\text{O}_{1.95}$  according to the database) two sets of diffraction lines, both belonging to silver were observed in the

diffraction pattern of the sample after the reaction cycle. One set of peaks belonged to silver in the cubic form the other one to silver in the hexagonal form. Both forms of silver crystals appeared in approximately equal amount; however the diffraction lines belonging to hexagonal form were rather sharp, whereas those belonging to cubic form were very broad. Most probably silver in the cubic structure may be ascribed to the observed nanocrystals (see Fig. 3).

The catalytic activity of the prepared electrodes in ORR was tested by EIS. Fig. 5 presents the dependence of the real part of the electrode impedance on frequency for LSM and Ag-LSM electrodes measured just after the preparation. The high frequency limit of the real part of the electrode impedance equals to the electrical resistance of the system. It is to be seen in Fig. 5 that the real part of the impedance at the high frequency for the Ag-LSM electrode amounted to approximately 40% of the real part of the impedance at the high frequency for the LSM electrode. The LSM electrode is a 3D electrode and its resistance is due mainly to the resistivity of the grain-grain contacts. Addition of silver, especially the presence of long silver needles (see Fig. 2 and 3) improves the electrical conductivity of the composite leading to the decrease of the high frequency resistivity. The low frequency limit of the real part of electrode impedance is equal to the polarization resistance of the electrode process (ORR). Also the low frequency limit of the real part of electrode impedance in the case of Ag-LSM electrode was much lower (approximately three times lower) than the low frequency limit of the real part of electrode impedance in the case of LSM electrode. It means that the addition of silver speeds up significantly the reaction of oxygen reduction on the LSM electrode. The experiments presented in Fig. 5 were done with the use of freshly prepared electrodes. It was checked however that the electrodes were relatively stable. During ten days of work the polarization resistance of the Ag-LSM electrode its polarization resistance grew up by 50%. Note however that the electrodes usually lose their activity after long work.

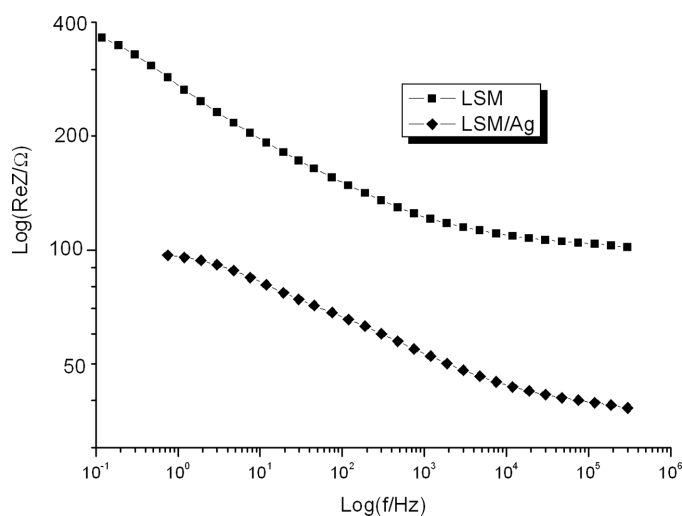


Fig. 5. The dependence of the logarithm of the real part of the electrode impedance on the logarithm of frequency for the LSM cathode (squares) and Ag-LSM cathode (diamonds) in the argon-oxygen atmosphere (10% oxygen) at the temperature 700°C

#### 4. Conclusions

The Ag-LSM composite to be used as a cathode in SOFCs may be successfully prepared by the procedure described in the present paper. The addition of silver to LSM improves both its conductivity as well as activity in ORR. Three types of silver were observed in the composite: big crystals, long needles and fine nanocrystals. Big Ag crystals probably play no role in the electrode behavior. We postulate that the long Ag needles increase the electrical conductivity of the composite by joining electrically the crystals of LSM, whereas fine nanocrystals, decorating the LSM crystals, decrease the polarization resistance of the electrode process increasing the three phase boundary, at which the reaction of oxygen reduction occurs.

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