Development of porous cathode powders for SOFC and influence of cathode structure on the oxygen electroreduction kinetics

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ABSTRACT

Mesoporous La1-xSrxCa0.33O1.48 powder with the specific surface area higher than 140 m² g⁻¹ has been synthesized from the corresponding nitrates, using solution thermal decomposition method. These nanopowders have been used for preparation of SOFC cathodes, demonstrating lower oxygen electroreduction activation energy than that for less porous cathodes prepared from the powders synthesized using traditional solid state reaction method. To increase macroporosity of the cathodes the special pore forming agent has been added into the raw cathode paste. The very low total polarization resistance and activation energy values have been obtained for oxygen electroreduction, depending on the cathode porosity and potential applied.

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1. Introduction

Solid oxide fuel cells working effectively at intermediate temperatures 773 < T < 973 K (ITSOFC) are being considered as the novel power generation devices in the near future because of very high chemical energy conversion efficiency and low pollution [1,2]. The oxygen electroreduction at/inside cathode and oxygen ion conductivity in the compact electrolyte are the rate limiting steps, if La1-xSr0.2MnO3-d and Zr1-xY2O3-d have been used [1–7]. To enhance the oxygen ion conductivity, the ceria based electrolyte Ce0.9Gd0.1O1.95 (CGO) cathode and Ni/CoO3 cermet anode [4–7], LSCO prepared using the traditional solid state reaction method (SSRM) is stable during thousands of working hours at T < 973 K [7].

The main objective of this study was to synthesize the fine LSCO nanopowders [3,8–10], using the nitrate solution thermal decomposition method (NSTDM) [3] to increase the contact area between cathode and electrolyte and catalytic activity of the cathode [7–10]. The second aim was to synthesize the cathodes with different macroporosity and to obtain the optimal concentration of the pore forming agent (PFA) in the raw cathode paste.

2. Preparation and characterization of materials and single cells

LSCO cathode powder was synthesized from La(NO₃)₃·6H₂O, Sr(NO₃)₂ (Aldrich, 99.9%) and Co(NO₃)₃·6H₂O (98%, Riedel-de Haën), using NSTDM [3,8–10]. The solution, prepared from corresponding salts, glycine as a reducing agent and Millipore water, was heated to form viscous solution and added drop-wise to a preheated Pt beaker (575...675 K). The solvent was quickly evaporated, the formed viscous liquid reacted autothermally to form the LSCO nanopowder [8–11] due to evolution of gases during highly exothermic reaction. The nanopowder was sintered during 8 h at fixed temperature T_sint (973...1523 K). XRD results show that the LSCO nanopowders sintered at T_sint > 1350 K have a very good crystallinity with the hexagonal cell (R-3c) lattice parameters given in Fig. 1a, differently from powders sintered at T_sint < 1200 K. The long-lasting sintering at higher temperatures is inevitable to give a good time stability of cathodes prepared from nanopowders [8–10]. Nitrogen adsorption and Brunauer–Emmett–Teller (BET) model have been used and the pore size distribution (PSD) and cumulative pore volume have been calculated using the non-local density functional theory [12]. Very high specific surface area S_BET > 140 m² g⁻¹ has been obtained and the mesopores with medium half pore width 15.6 Å prevail at the surface of LSCO powder sintered at 1423 K (Fig. 1b). Based on XRD and BET data, the noticeably wider PSD is obtained for LSCO sintered at 1200 K, having amorphous structure.

The raw cathode paste was prepared by adding ethyl cellulose, PFA (0–10 wt% of the paste), ethanol and turpentine oil to the LSCO nanopowder and laminated onto the Ce0.9Gd0.1O1.95 (CGO) electrolyte surface under small overpressure and thereafter sintered at T_sint > 1323 K during 5 h. SEM data show that the macroporosity of the cathode, V_m, depends strongly on wt% of PFA. The Pt/TiO₂ reference electrode was created inside the electrolyte [7–10].

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CGO powder with $S_{BET} = 19.9 \text{ m}^2 \text{ g}^{-1}$ (NexTech Materials) was pressed at 90 MPa into the disc (diameter 2.4 cm) and sintered at 1773 K during 8 h. $S_{BET}$ of electrolyte was negligible and the root mean square roughness $R_{ms} = 58 \text{ nm}$ has been obtained using AFM. The Pt-paste was tapecast onto the LSCO cathode and CGO electrolyte at the room temperature and sintered at 1173 K during 900 s. AFM data show that there are macropores inside the cathode with diameter from 0.5 $\mu$m to 5.0 $\mu$m and the diameter of big monograin particles varies from 2 $\mu$m to 5 $\mu$m. BET analysis shows that there are mesopores with medium radius $R_P \approx 13.0 \text{ Å}$, $S_{BET} \approx 6 \text{ m}^2 \text{ g}^{-1}$ and $V_{tot} > 26\%$. $S_{BET}$ depends somewhat on PFA wt%, being maximal ($S_{BET} = 7.8 \text{ m}^2 \text{ g}^{-1}$; $V_{tot} \approx 31\%$) at 1.36 wt% addition of PFA. $R_{ms} \approx 800 \text{ nm}$ for LSCO sintered at 1373 K during 5 h, and increasing $T_{sint}$ causes the decrease in $R_{ms}$.

3. Results of electrochemical studies

Current density for single cells, $j$, depends noticeably on the porous structure of the cathode, i.e. on PFA wt% (maximal $j$ has been measured at 1.36...2.67 wt%). Current exceeds by a factor of 3...4 the current achieved for LSCO prepared using SSRM [7–10]. There is no big hysteresis in $j$ vs. electrode potential ($\Delta E$) curves if PFA amount exceeds 2.67 wt%, hence, the mass transfer characteristics depend somewhat on the macroporosity of the cathode.

The shape of Nyquist (Fig. 2) and Bode plots [13] (not shown for shortness) also depends noticeably on PFA wt%. The lowest total polarization resistance $R_p$ (Fig. 2c) has been obtained at 1.36 wt% of PFA addition ($S_{BET} = 7.8 \text{ m}^2 \text{ g}^{-1}$; $V_{tot} \approx 31\%$). The Nyquist plots have been normalized for the better kinetic analysis (the uncorrected values of the electrolyte resistance $R_{el}$ depend on PFA wt% and $R_{el}$ is minimal at 1.36 wt%).

In Nyquist plots at $T > 873$ K (PFA content $\geq 2.67$ wt%) there is only one very well visible semicircle with corresponding high characteristic relaxation time constant $\tau_{max} = (2\pi f_{max})^{-1}$ ($f_{max}$ is the frequency of the maximum in the $Z'Z''$ plots). $r_{max}$ varies from 0.11 s to 0.13 s, differently from cathode without PFA (0.18 < $r_{max}$ < 0.20 s). $r_{max}$ decreases with increasing temperature ($r_{max} = 0.025 \text{ s}$ at $T = 973$ K), but is independent of electrode potential $\Delta E$ applied.

The Nyquist and Bode plots at $T \leq 813$ K can be fitted by the equivalent circuit (EC, Fig. 3a), where the low-frequency process (electroreduction of $O_2$ inside mesopores) is characterized with constant phase element impedance $Z_{CPE}$ and charge transfer resistance $R_t$, and high-frequency electroreduction of $O_2$ at more open surface areas is simulated with capacitance $C_t$ and resistance $R_1$. Very high electrical double layer capacitance and constant phase
element coefficient $A_2$ (Fig. 3), indicating the accumulation of partially reduced oxygen species inside the porous cathode structure, and very low values of charge transfer resistances $R_1$ (not shown) and $R_2$ (Fig. 3) have been obtained. $R_1$ depends only weakly on PFA wt%, however, $R_2$ depends on PFA wt%, being maximal at 1.36 wt% and indicating that the optimal macro-porosity of the cathode is very important.

The effect of the high frequency process is negligible at PFA $> 0.21$ wt% and at $T = 873$ K (Fig. 2b) EC simplifies and only $R_{el}, R_2$ and CPE$_2$ are important. However, a better fit can be obtained if CPE$_2$ element has been exchanged to the generalized short circuit Warburg diffusion impedance $Z_W$ (EC in Fig. 4a). Modified EC includes also additional charge transfer resistance $R_1$ and $C_1$ elements, depending on PFA wt% (Fig. 4a,c). Diffusion resistance $R_D$ (Fig. 4b) depends on $A\Delta E$, indicating that $R_D$ is not a simple diffusion process resistance and, in addition to diffusion, the migration of $O^2-$ anions, surface diffusion etc. are important at $A\Delta E \neq 0$ [7–10].

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**Fig. 3.** Dependence of the low-frequency CPE$_2$ coefficient $A_2$ (a), $C_1$ (b) and low-frequency charge transfer resistance $R_2$ (c) on $A\Delta E$ at various additions of PFA (wt%), given in figure. EC used for fitting of Nyquist plots is given in figure.

**Fig. 4.** Dependence of fitting parameters $R_1$ (a), $R_D$ (b) and $C_1$ (c) on the cathode potential $A\Delta E$ at $T = 873, 923$ and 973 K and at fixed addition of PFA (wt%), given in figure.

**Fig. 5.** Dependence of activation energy on $A\Delta E$ at various additions of PFA (wt%), given in figure.
The activation energy $E_{\text{act}}$ for oxygen reduction (Fig. 5) depends noticeably on $S_{\text{BET}}$ and porosity of the cathode (the lowest $E_{\text{act}}$ has been achieved for 1.36 wt% of PFA). However, there is no linear dependence of $E_{\text{act}}$ on $S_{\text{BET}}$ or $V_{\text{tot}}$ of the cathode, and more information is needed to give the detailed analysis.

The time stability of the single cell characteristics is reasonable during hundreds of hours and the long-lasting performance stability studies are in progress in our laboratory now.

4. Conclusions

Porous La$_{1-x}$Sr$_x$CoO$_{3-d}$ powder with the specific surface area higher than $S_{\text{BET}} = 140 \text{ m}^2 \text{ g}^{-1}$ has been synthesized and used for preparation of the highly active cathodes ($S_{\text{BET}} > 6 \text{ m}^2 \text{ g}^{-1}$) for the intermediate temperature SOFCs. The addition of pore forming agent (PFA) into the raw cathode material increases mainly macroporosity and $S_{\text{BET}}$ of the cathodes. The mesopore volume and pore size distribution only slightly change in comparison with a diameter of the nanopowder particles used. Very low total polarization resistance for oxygen electroreduction ($R_p \leq 0.03 \text{ X ohm cm}^2$ at 873 K) has been obtained for 1.36 wt% of PFA. The total activation energy for oxygen electroreduction depends on the meso- and macroporosity of the cathodes, and the lowest $E_{\text{act}}$ (> 0.5 eV at open circuit potential) has been obtained for LSCO with total porosity of 31% and $S_{\text{BET}} = 7.8 \text{ m}^2 \text{ g}^{-1}$, i.e. with 1.36 wt% PFA. However, there is no linear dependence of $E_{\text{act}}$ on $S_{\text{BET}}$, indicating that $R_p$ depends crucially on the active surface area, macroporosity and electronic conductivity of the cathode synthesized.

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