

Electrode behavior in intermediate-temperature SOFCs with lanthanum gallate- and silicate-based electrolytes

E.V.Tsipis^{1,2}, V.A. Kolotygin², V.V.Kharton²

¹ *Chemistry Department, Instituto Tecnológico e Nuclear, CFMC-UL, Estrada Nacional 10, 2686-953 Sacavém, Portugal*

² *Department of Ceramics and Glass Engineering, CICECO, University of Aveiro, 3810-193 Aveiro, Portugal
mail: katya@itn.pt*

The high level of oxygen ionic conductivity in the solid electrolytes based on perovskite-type lanthanum gallate and apatite-type silicate, in particular $\text{La}_{1-x}\text{Sr}_x\text{Ga}_{1-y}\text{Mg}_y\text{O}_{3-\delta}$ (LSGM) and $\text{La}_{10-x}(\text{Si}_{1-y}\text{Al}_y)_6\text{O}_{26\pm\delta}$ (LSAO), enables their use for intermediate-temperature solid oxide fuel cells (IT SOFCs) operating at 870-1070 K. Reducing of SOFC operation temperature is associated, however, with increasing role of electrode polarization as a performance-limiting factor, since the apparent activation energy for the polarization resistance is typically higher than that for ionic transport in solid electrolytes. The electrochemical activity of conventional electrode materials, such as lanthanum-strontium manganites as cathodes and cermets containing yttria-stabilized zirconia (YSZ) as anodes, may become insufficient at temperatures below 1050 K. Therefore, an important aspect in the IT SOFC developments is the search for new electrode materials. In the present study, the electrochemical activity of selected cathode and anode materials was appraised for the cells based on gallate and silicate electrolytes. Apart from the electrode performance, special emphasis was given also to the other properties important for potential applications in SOFCs, including the partial electronic and ionic conductivities in a wide range of the oxygen partial pressure, oxygen permeability, phase stability, thermal and chemically-induced expansion as well as chemical interaction and cation interdiffusion processes between the electrode and electrolyte. One particular goal was to assess possible correlations between the transport properties of electrode and electrolyte materials and electrochemical behavior and to reveal other factors limiting the electrode performance.

Comparative studies of the cathodic behavior were carried out using a series of model mixed-conducting compositions, which included $\text{Ln}_2(\text{Ni,Cu})\text{O}_{4+\delta}$ ($\text{Ln} = \text{La, Pr}$) with K_2NiF_4 -type structure, recently discovered intergrowth $\text{YBaCo}_4\text{O}_{7+\delta}$, perovskite-type $(\text{La}_{0.75}\text{Sr}_{0.25})_{0.95}\text{Cr}_{0.5}\text{Mn}_{0.5}\text{O}_{3-\delta}$ (LSCM) and $\text{SrMn}_{0.5}\text{Nb}_{0.5}\text{O}_{3-\delta}$, and various oxide composites comprising fluorite-type $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{2-\delta}$ (CGO) and perovskite-type $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_{3-\delta}$ (LSM) or $\text{La}_{0.8}\text{Sr}_{0.2}\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_{3-\delta}$ (LSFC). In all cases, the polarization resistance of porous cathodes in contact with apatite-type $\text{La}_{10}\text{Si}_5\text{AlO}_{26.5}$ solid electrolyte at 873-1073 K in air was found substantially higher compared to similar layers applied onto $(\text{La}_{0.9}\text{Sr}_{0.1})_{0.98}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{3-\delta}$. For the nickelate- and cobaltite-based cathodes with high electronic conduction, the apparent activation energies (E_a) for the so-called electrode conductivity are close to the E_a values for ionic transport in LSGM and LSAO, 65-85 kJ/mol. The relatively low electrode performance in LSAO-supported cells is primarily associated with the surface diffusion of silica from $\text{La}_{10}\text{Si}_5\text{AlO}_{26.5}$, which partially blocks the electrochemical reaction zone without formation of secondary phases detectable by X-ray diffraction (XRD). Nonetheless, traces of SiO_2 -containing phases were identified by energy-dispersive spectroscopy (EDS) coupled with transmission and scanning electron microscopy (TEM/SEM). The oxygen reduction kinetics was also found strongly influenced by the transport properties of solid electrolyte and by the exchange-related processes at the electrode surface. The role of the latter factor becomes evident on increasing current density and in the cases when ionic conductivity of the electrode materials is low. Porous YBaCo_4O_7 -based cathodes show a very high electrochemical activity

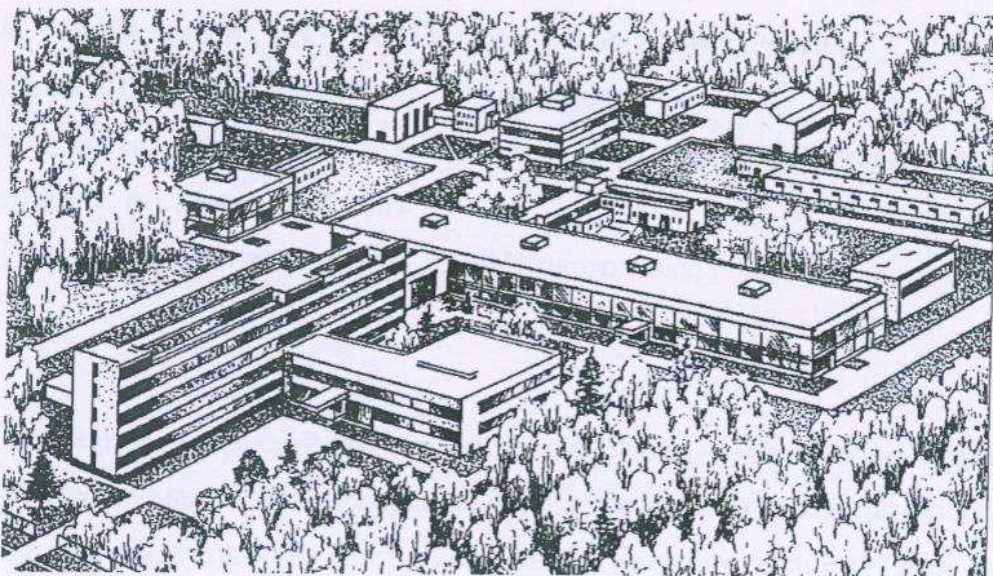
in contact with LSGM at 873-1073 K, the temperature range comprising thermodynamic stability boundary of the layered cobaltite. On the contrary, the performance of manganite- and chromite-based cathodes such as LSCM is relatively poor; their electrochemical behavior suggests a key role of electronic transport-related processes. The cathode performance can be improved by incorporating electrocatalytically-active components, such as metallic Ag, praseodymium oxide or nickelate, and CGO interlayers. As an example, at 873 K, the surface modification with praseodymium oxide decreases overpotential of $\text{La}_2\text{Ni}_{0.8}\text{Cu}_{0.2}\text{O}_{4+\delta}$ cathode screen-printed onto LSGM and annealed at 1473 K, from 330 down to approximately 175 mV at 50 mA/cm^2 . In addition to the optimization of electrode composition and microstructure, positive effects were also achieved by reducing electrode fabrication temperature until a sufficient mechanical strength is kept, and by optimizing current collection.

The model anodes studied in this work, included primarily a series of dual- and triple-phase cermets containing Ni, Cu, Co, Ag and Pt metals. The oxide components in the cermets were selected from various solid electrolytes, mixed conductors and insulating materials, such as 8% yttria-stabilized zirconia (Y8SZ), $\text{CeO}_{2-\delta}$, CGO and $\text{TbZrO}_{4-\delta}$ with fluorite-related structure, zircon-type $\text{Ce}_{0.8}\text{Ca}_{0.2}\text{VO}_{4+\delta}$, pyrochlore $\text{Gd}_{1.86}\text{Ca}_{0.14}\text{Ti}_2\text{O}_{7-\delta}$ (GCTO), perovskite-type LSCM and $\text{La}_{0.9}\text{Sr}_{0.1}\text{Al}_{0.65}\text{Mg}_{0.15}\text{Fe}_{0.20}\text{O}_{3-\delta}$, and Al_2O_3 -containing additives incorporated in order to test possible silica-scavenging effects. The comparative studies of porous anode layers deposited onto LSGM and LSAO solid electrolytes were performed in H_2 - H_2O - N_2 atmospheres using impedance spectroscopy and measurements of the overpotential-current dependencies in combination with XRD, TEM/EDS and SEM/EDS analyses. LSCM and its derivatives were also tested as materials for all-ceramic anodes comprising one or several porous layers. The best performance in H_2 - H_2O - N_2 atmospheres was found for the electrode layers comprising at least one dimensionally-stable electrolyte component (e.g. Y8SZ or GCTO), one Ce-containing phase (e.g. CGO or cerium vanadate), and one metallic phase providing a sufficiently high electronic transport. The ionic conductivity of the oxide components seems less significant with respect to redox stabilization and catalytic activity, whilst interaction between the materials decreases the anode performance. As for the porous cathodes, silica poisoning of the anode surface and blocking of the triple-phase boundary in the electrochemical cells with apatite-type solid electrolytes plays the most critical role. For the LSGM-supported cells, the materials interdiffusion and incorporation of transition metal cations into the lanthanum gallate surface also influences electrode behavior, but this effect is less pronounced with respect to other performance-limiting factors.

Российская академия наук
Научный совет РАН по физике конденсированных сред
Российский фонд фундаментальных исследований
Фонд содействия развитию малых форм предприятий в научно-
технической сфере
Учреждение Российской академии наук Институт физики твердого
тела РАН

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