

Al_{0.04}Sc_{0.06}Zr_{0.9}O_{1.95} kietojo elektrolito impedanso spektrų modeliavimas ekvivalentine grandine ir analizė DRT metodu

Impedance spectra of Al_{0.04}Sc_{0.06}Zr_{0.9}O_{1.95} solid electrolyte analysed by DRT method and equivalent circuit modelling

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Zirconia based oxygen conductors are state of the art solid electrolytes for solid oxide fuel cell applications [1]. In order to achieve high ionic conductivity, the most promising doping of ZrO₂ is by Sc₂O₃ and Al₂O₃ [2, 3]. In the present work we focus our investigation on double doped zirconia by aluminum oxide and scandium oxide. The Al_{0.04}Sc_{0.06}Zr_{0.9}O_{1.95} electrolyte was prepared via Pechini method. In the temperature range 300-800 K, the structure of this material is cubic with some fraction of monoclinic modification, while above 800 K a phase transforms to purely cubic.

The Al_{0.04}Sc_{0.06}Zr_{0.9}O_{1.95} electrolyte in the form of ceramics was investigated by broadband impedance spectroscopy in the frequency range from 0.03 Hz to 8 GHz and in temperature interval from 300 to 980 K. The equivalent circuit analysis and distribution of relaxation times (DRT) techniques were used to analyze impedance spectra. Three kinds of relaxation processes are clearly distinguishable on impedance spectra. The first process is observed in low frequency range at lower temperatures (400 K) and it moves continuously through the entire frequency interval up to GHz range with temperature increase. This charge carriers relaxation process is located within ceramic grains. At high temperatures, in Hz diapason, the second very strong relaxation process is observed. This relaxation process of charge carriers is located at the sample - electrode interface. In frequencies in between of grain process and interface process a third relaxation process is observed, which is related to ceramics grain boundaries.

The DRT peaks were described by Gaussian probability density functions. The relaxation, which was attributed to the bulk relaxation process, was a dual peak at low temperatures, meanwhile it became a single relaxation process at higher temperatures. The complexity of high frequency relaxation process observed in the DRT representation of the spectra at temperatures up to 500 K was associated with two zirconia phases.

The temperature dependencies of conductivities and

relaxation times show interesting behaviour. The relaxation process, which was related to monoclinic phase, is governed by the relaxation process related to cubic phase above 500 K. Still the activation energy of grain relaxation process associated to cubic phase changes in the vicinity of phase transition, which points out, that cubic phase in the temperature region below and above 800 K (which is a phase transition temperature) is not the same. X-ray diffraction data shows some small change of crystal lattice size. This may be a reason for changing of potential relief and consequently the activation energy for mobile ions during this phase transition.

Our study shows that the activation energies, corresponding to the observed relaxation processes, can be determined more accurately from the DRT analysis as compared to equivalent circuit modelling of impedance data.

A laboratory fuel cell based on Al_{0.04}Sc_{0.06}Zr_{0.9}O_{1.95} as an electrolyte membrane (0.8 mm thick) was demonstrated. Ni-Al_{0.04}Sc_{0.06}Zr_{0.9}O_{1.95} cermet was used as the anode and two layers were used as cathode – the first one Al_{0.04}Sc_{0.06}Zr_{0.9}O_{1.95}-LSM composite and the second one LSM. The fuel cell gives ~206 mW cm⁻² of power at 1123 K.

Keywords: solid electrolyte, impedance spectroscopy, ionic conductivity, distribution of relaxation times, solid oxide fuel cell.

Literature

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