OXYGEN IONIC AND ELECTRONIC TRANSPORT IN APATITE CERAMICS

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Development of novel solid electrolytes with oxygen ionic conductivity is of great interest for high-temperature electrochemical applications, including solid oxide fuel cells (SOFCs), oxygen pumps, electrolyzers and sensors. This work was focused on the study of ionic and electronic transport in apatite-type $La_{9.83}Si_{4.5}Al_{1.5-y}Fe_yO_{26}$ (y= 0-1.5), $La_{9.83-x}Pr_xSi_{4.5}Fe_{1.5}O_{26}$ (x= 0-6), $La_{10-x}Si_{6-y}Fe_yO_{26\pm\delta}$ (x= 0-0.77; y= 1-2) and $La_{7-x}Sr_3Si_6O_{26-\delta}$ (x = 0-1). Single-phase apatite ceramics with 96-99% density were prepared by the standard solid-state synthesis route and characterized by XRD, SEM/EDS, dilatometry, impedance spectroscopy, determination of oxygen ion transference numbers by faradaic efficiency and e.m.f. methods, and Mössbauer spectroscopy, and measurements of total conductivity and Seebeck coefficient vs. oxygen partial pressure. The ionic conductivity of apatite phases was found to increase with oxygen content. In air, the ion transference numbers at 973-1223 K are close to unity for $La_{9.83}Si_{4.5}Al_{1.5-y}Fe_yO_{26+\delta}$ and $La_{10}Si_5FeO_{26.5}$, and vary in the range 0.96-0.99 for other compositions. Doping of $La_{9.83}(Si,Al)_6O_{26+\delta}$ with iron results in increasing Fe^{4+} fraction, which correlates with partial ionic and p-type electronic conductivities, whereas La-stoichiometric $La_{10}(Si,Fe)O_{26+\delta}$ and Pr-containing apatites stabilize trivalent iron state. Among the studied materials, the highest ionic and electronic transport is observed for $La_{10}Si_5FeO_{26.5}$, where oxygen interstitials are close neighbors of Si-site cations. The ionic conduction in substituted apatites remains dominant under SOFC operation conditions, although doping with variable-valence cations, such as iron and praseodymium, moderately increase the p- and n-type electronic conductivities. However, reducing $p(O_2)$ leads to a drastic decrease in the ionic transport, presumably due to transition from prevailing interstitial to a vacancy diffusion mechanism, which is similar to the effect of acceptor doping. Iron additions were found to improve the sinterability of silicate ceramics. Thermal expansion coefficients of apatite solid electrolytes in air are $(8.8\text{-}14.7)\times10^{-6}$ K^{-1} at 300-1250 K.