IONIC AND N-TYPE ELECTRONIC CONDUCTION

IN $La_2Mo_2O_9$-BASED SOLID ELECTROLYTES

I.P. Marozau[a], A.L. Shaula[b], V.V. Kharton[b], A.P. Viskup[a], J.R. Frade[b], F.M.B. Marques[b]

[a] Institute of Physicochemical Problems, Belarus State University, 14 Leningradskaya Str., 220050 Minsk, Belarus
[b] Department of Ceramics and Glass Engineering, CICECO, University of Aveiro, 3810-193 Aveiro, Portugal

Solid electrolytes based on lanthanum molybdate possess a substantially high oxygen ionic conductivity and may thus be of interest for high-temperature electrochemical applications. The present report summarizes data on physicochemical and transport properties of $La_{1.7}Bi_{0.3}Mo_2O_9$, $La_2Mo_{1.7}W_{0.3}O_9$ and $La_2Mo_{1.95}V_{0.05}O_9$ ceramics, which were reported among most-conducting materials derived from $La_2Mo_2O_9$. The partial oxygen ionic and n-type electronic conductivities of lanthanum molybdate-based solid electrolytes were studied at 973-1173 K in the $p(O_2)$ range from 10^{-5} to 1.0 atm by impedance spectroscopy, faradaic efficiency and e.m.f. methods. The oxygen ion transference numbers are 0.995-0.977 in air, decreasing when the oxygen partial pressure decreases or temperature increases. Under the $p(O_2)$ gradient of $0.21/10^{-5}$ atm, the n-type electronic contribution to the total conductivity achieves 5-20% at 1123-1173 K. Reducing $p(O_2)$ down to 10^{-4}-10^{-3} atm leads to a reversible degradation of the total conductivity, probably due to phase decomposition. The activation energies for ionic and electronic transport in air vary in the ranges 61-71 and 123-141 kJ/mol, respectively. Doping $La_2Mo_2O_9$ with calcium results in the segregation of $CaMoO_4$-based solid solution, accompanied with increasing electronic conductivity. The average thermal expansion coefficients of $La_2Mo_2O_9$-based ceramics in air are $(14.4 - 14.8) \times 10^{-6}$ K^{-1} at 300-700 K, and increase up to $(16.4 - 22.5) \times 10^{-6}$ K^{-1} at higher temperatures.