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Ionic-electronic transport in zircon-type $PrVO_4$-based ceramics

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$LnVO_4$ orthovanadates attract attention as prospective materials for electrochemical applications, in particular, as redox-reversible electrode components for solid oxide fuel cells (SOFC).[1,2] One important advantage of $LnVO_4$-derived components of SOFC anodes is their prospective good resistance to carbon deposition and sulphur-containing impurities which is critical for hydrocarbon-fueled SOFCs. The present work was focused on the impact of the acceptor-type substitution by calcium on the electrical transport properties of zircon-type orthovanadate $PrVO_4$ under oxidizing conditions.

Undoped $PrVO_4$ and calcium-substituted $Pr_{1-x}Ca_xVO_{4-\delta}$ (x = 0.02-0.20) were prepared by conventional solid state route and sintered at 1300°C for 5h in air. The prepared materials were characterized by X -ray and neutron diffraction, SEM/EDS, thermal analysis, and measurements of electrical properties in controlled atmospheres. XRD demonstrated the formation of phase-pure solid solutions with tetragonal zircon-type structure for up to 5 at. % of calcium in Pr sublattice, while SEM/EDS suggest a lower solubility due to the presence of Ca-V-O phase impurities. $Pr(Ca)VO_4$ ceramics showed semiconducting behavior under oxidizing conditions at 400-900°C. Within the solubility range, doping with calcium increases the total conductivity. The ionic and electronic contributions at 700-900°C were assessed by the modified e.m.f. technique. The electronic conductivity is p-type and decreases with decreasing $p(O_2)$. At lower temperatures, the total conductivity was found to be higher in wet atmospheres compared to dry conditions, thus implying a significant contribution of protonic transport at temperature below 550°C. The redox behavior of $PrVO_4$-based ceramics on isothermal cycling between air and 10%H_2-N_2 was studied by impedance spectroscopy, thermogravimetry and XRD analysis.

References:

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