Non-stoichiometry in oxide thin films operating under anodic conditions: A chemical capacitance study of the praseodymium-cerium oxide system

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Abstract:

$Pr_xCe_{1-x}O_{2-\delta}$ can potentially serve as both a cathode and anode in solid oxide fuel cells given that it exhibits significant mixed ionic-electronic conductivity (MIEC) under both cathodic and anodic conditions. While MIEC depends strongly on oxygen nonstoichiometry δ, there have been few ways to extract this information reliably and *in situ*, particularly for thin films. In this work, this is achieved by analysis of chemical capacitance values extracted from impedance spectroscopy data obtained on electrochemical cells of the form $Pr_{0.1}Ce_{0.9}O_{2-\delta}$ / $Y_{0.16}Zr_{0.84}O_{1.92}$ / $Pr_{0.1}Ce_{0.9}O_{2-\delta}$ operating at temperatures between 450 to 700°C and over the pO_2 range of 10^{-33}-10^{-14} atm. In combination with our prior investigation, the stoichiometry over a very wide pO_2 range is demonstrated. The themodynamic factor, relevant to the analyses of diffusivity D and exchange coefficient k derived by various experimental routes, is calculated over a wide temperature and pO2 range and discussed in relation to published experimental data.