The Formation of Performance Enhancing Pseudo-Composites in the Highly Active La$_{1-x}$Ca$_x$Fe$_{0.8}$Ni$_{0.2}$O$_3$ System for IT-SOFC Application

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The La$_{1-x}$Ca$_x$Fe$_{0.8}$Ni$_{0.2}$O$_3$–$\delta$($0 \leq x \leq 0.9$) system is investigated for potential application as a cathode material for intermediate temperature solid oxide fuel cells (IT-SOFCs). A broad range of experimental techniques have been utilized in order to elucidate the characteristics of the entire compositional range. Low A-site Ca content compositions ($x \leq 0.4$) feature a single perovskite solid solution. Compositions with 40% Ca content ($x = 0.4$) exhibit the highest electrical and ionic conductivities of these single phase materials (250 and $1.9 \times 10^{-3}$ S cm$^{-1}$ at 800 °C, respectively), a level competitive with state-of-the-art (La,Sr)(Fe,Co)O$_3$. Between 40 and 50% Ca content ($0.4 > x > 0.5$) a solubility limit is reached and a secondary, brownmillerite-type phase appears for all higher Ca content compositions ($0.5 \leq x \leq 0.9$). While typically seen as detrimental to electrochemical performance in cathode materials, this phase brings with it ionic conductivity at operational temperatures. This gives rise to the effective formation of pseudo-composite materials which feature significantly enhanced performance characteristics, while also providing the closest match in thermal expansion behavior to typical electrolyte materials. This all comes with the advantage of being produced through a simple, single-step, low-cost production route without the issues associated with typical composite materials. The highest performing pseudo-composite material ($x = 0.5$) exhibits electronic conductivity of 300–350 S cm$^{-1}$ in the 600–800 °C temperature range while the best polarisation resistance ($R_p$) values of approximately 0.2 Ωm$^2$ are found in the 0.5 ≤$x$≤0.7 range.