

Mixed Conductivity of Strontium Yttrium Titanate at Low Oxygen Pressure

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We have developed a ceramic material based on SrTiO₃ with an electronic conductivity up to 80 S/cm and substantial oxygen ion conductivity under reducing conditions at 800°C. It can be cycled between oxidizing and reducing environments without loss of mechanical integrity. Its thermal expansion and chemical properties are compatible with zirconia or ceria electrolytes. It may find application as a mixed conducting ceramic fuel cell anode.

SrTiO₃ has the ideal cubic perovskite structure. Its conductivity at 800°C is near 10⁻⁵ S/cm in air due to acceptor impurities. Donor doping of the A-site by lanthanide or yttrium ions increases the conductivity by several orders of magnitude. As oxygen pressure is decreased, the conductivity initially decreases until a cross-over to n-type conduction, then increases. Although the large ions, La - Nd, are completely soluble in SrTiO₃, the smaller lanthanides are more effective in generating conduction electrons and the most effective is yttrium. The solubility of Y in SrTiO₃ is near 8 mol% and the conductivity of this composition at 800°C is over 60 S/cm at a P_{O₂} of 10⁻¹⁹ atm. This compares to values of less than 15 S/cm for any of the other dopants.

SrTiO₃ exhibits a fair degree of non-stoichiometry and the side containing Sr vacancies is of greater importance in this application. In order to make the Y-doped compound, extra Sr is removed to compensate for the charge difference between Y and Sr ions, creating A-site vacancies. Thus the composition at the maximum solubility of yttrium is Sr_{0.88}Y_{0.08}TiO₃ and has a corresponding conductivity of 63 S/cm at 800°C. However, by further increasing the Sr deficiency to Sr_{0.86}Y_{0.08}TiO₃, the conductivity increases to over 80 S/cm.

Doping of 5% transition metal ions on the B-site, i.e., substituting for Ti, results in a decrease in conductivity. Of the transition metals, cobalt and manganese are least deleterious ($\sigma = 35$ S/cm) and Cr and Zn have the most deleterious effect on conductivity. However, this is partially offset by an increase in Y solubility when B-site acceptor dopants are present. For example, the conductivity of Sr_{0.85}Y_{0.10}Ti_{0.95}Co_{0.05}O₃ is 45 S/cm.

The ionic conductivity of SrTiO₃ has not been measured independent of the electronic conductivity. An upper estimate of log σ_i from the minimum in the plot of log σ_i versus P_{O₂} at 800°C is in the range -4.5 to -2 for undoped to highly doped SrTiO₃. As such, SYT possesses useful characteristics for an anode material wherein the oxidation reaction can occur over the entire surface, rather than only at the triple phase boundary as in Ni-YSZ. The catalytic performance of this material has not been evaluated.

Although a number of single phase ceramics have been considered in the past as anodes for solid oxide fuel cells, none of them have proved viable. Materials such as (La,Ca)CrO₃, (Ti,Nb)O₂, and Sm₂(Ti,Nb)₂O₇ have insufficient conductivity under normal fuel cell operating conditions. The same is true of La-doped SrTiO₃, unless high-purity gases with strong reducing potentials are used. Gd₂(Ti,Mo)₂O₇ exhibits a conductivity near 70 S/cm over a limited range of reduced oxygen pressure at 800°C, but is unstable at higher or lower pressures. Thus Y-SrTiO₃ is the first material with sufficient electronic conductivity over a broad range of temperature (600 - 1000°C) and oxygen pressure (10⁻¹⁴ - 10⁻²⁰ S/cm) and adequate ionic conductivity to be suitable for a fuel cell anode.