

Superionic conductors for solid oxide fuel cells: structure-bulk property relationships in Bi₂O₃ based solid solutions

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Solid oxide fuel cells (SOFCs) are electrochemical devices that convert chemical energy directly to electrical energy with reduced CO₂, SO₂ and NO_x emissions [1]. They are highly efficient and when operated in combined heat and power mode they can reach efficiencies above 80% [2]. These devices have been known since Bauer and Preis reported their first use to produce electricity in 1937 [3]. Over 100 years have passed but no large scale production of such efficient devices have been achieved. The main problem is the high temperature at which they operate (800-1000°C). The operation temperature is mainly determined by the electrolyte; an oxide ion conducting ceramic that rely largely on thermally activated oxide ion hopping mechanism (vacancy mechanism) for ionic transport. The state of the art electrolyte is yttria-stabilized zirconia (YSZ). YSZ has conductivities ranging between 0.01 Scm⁻¹ and 0.1 Scm⁻¹ at 800°C and 1000°C respectively [4]. These high temperatures require the use of expensive materials with high melting points such as doped LaCrO₃ for interconnects.

Electrolytes that show promise are the solid solutions of Bi₂O₃. Bi₂O₃ in its fluorite δ -phase is highly defective, with 25% of the oxygen sites vacant and is reported to have conductivities of about 1 Scm⁻¹ at 730 °C, the highest for an oxide ion conducting ceramic reported thus far [5]. Unfortunately, the δ -phase is only stable within a narrow temperature range of 730-824°C [6]. Below this range, a monoclinic α -phase exist which is predominantly an electronic conductor and Bi₂O₃ melts at 825°C [7]. To stabilize the highly conductive defect fluorite phase, isovalent and aliovalent cations have been used to substitute for the Bi³⁺ cation in the structure. In our work, we have fabricated solid solutions of Bi₂O₃ using the double and triple doping strategies. We have also followed crystal phase changes and measured conductivities with variable temperature XRD and electrochemical impedance spectroscopy respectively. The local environment was probed with variable temperature Raman spectroscopy. This enables us to study the cubic phase and get insight into the structure-property correlations of materials reported to have high conductivities.

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