

ION CONDUCTING CERAMIC
ELECTROLYTES:
A CENTURY OF PROGRESS

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The evolution of sodium, oxygen and hydrogen ion conducting ceramic electrolytes will be traced with particular attention given to oxygen ion conductors. At the beginning of the 20th century, scientists began investigations on polycrystalline ceramic electrolytes. In 1916 beta-alumina (β - Al_2O_3) containing ~ 10 mol % Na_2O was discovered. It was used commercially as a glass-furnace refractory before it was 'rediscovered' to be a good sodium ion conductor with an ionic conductivity at 300 °C of ~ 0.07 S/cm (1). β "- Al_2O_3 was subsequently discovered with a higher Na_2O concentration (~ 13 mole %) and with a significantly higher sodium-ion conductivity of ~ 0.25 S/cm. Furthermore, oxides such as Li_2O or MgO in solid solution and at concentrations of ~ 2.6 and ~ 10 mole %, respectively, were required to stabilize the β "- Al_2O_3 phase during sintering/annealing and also to enhance the sodium ion conductivity (1,2). The cation dopants (Li^+ and/or Mg^{2+} substituting for Al^{3+}) are compensated electrically by mobile interstitial sodium ions situated in two-dimensional conduction planes in the structure. By the early seventies, thin-walled β "- Al_2O_3 electrolyte tubes could be fabricated with acceptable ionic conductivities, negligible electronic conductivity, sufficient mechanical strength, and electrochemical stability and durability in the presence of liquid sodium and sodium polysulfide (2). Ford Motor Company announced the commercial feasibility of the Na/S energy storage battery. Since that time, successful pilot-plant developments of rechargeable Na/S and Na/NiCl₂ batteries for electric vehicles (15-130 kWh) and load-leveling energy storage systems (up ~ 8 MWh in size) have taken place in the United States, Great Britain, Germany, and Japan (1,2).

Yttria-stabilized zirconia (YSZ) is currently the electrolyte of choice in many electrochemical systems (3). It was developed in about the same time frame as the conductive β "- Al_2O_3 ceramic (2). Oxides based on ZrO_2 were found to exhibit attractive oxygen ion conductivities (i.e. ≥ 0.02 S/cm @ 900-1000 °C) in 1900. Oxygen ion vacancies are the mobile species carrying the ionic current. They are generated in the crystal lattice by the solid solution of trivalent and divalent cations (e.g. Ca^{2+} or Y^{3+} substituting for Zr^{4+}), which also stabilize the material in the ion-conducting, cubic-fluorite structure. Over the years, extensive electrochemical studies have been conducted on the characterization of stabilized zirconia and other closely related electrolytes which have included (i) establishing the relationship between oxygen ion diffusivity and conductivity via the Nernst Einstein relation, (ii) measurement of oxygen ion and electron/hole conductivities as a function of stabilizer type and composition, temperature and oxygen partial pressure, and (iii) characterization of oxygen permeation and the ionic conducting (or electrolytic) regime (2,3).

In the sixties and seventies, Brown Boveri in Germany and Westinghouse in the United States demonstrated that commercially attractive power densities could be achieved in the SOFC, providing cell components in appropriate configurations with optimal properties were utilized. Subsequently, large development efforts have been underway in the United States, Germany, and Japan (2,3,4). Prototype SOFC power systems several hundred kilowatts in size and with sealless tubular cell designs employing YSZ electrolytes have been manufactured and tested successfully (4).

Electrolytes with higher conductivities (stabilized ceria and Bi_2O_3 ; Sr/Mg doped LaGaO_3) and protonic conducting perovskites or mixed perovskites are potential alternatives to YSZ (2,3). The evolution of SOFC designs from tubular cells utilizing electrolytes with thick walls (~ 500 μm) to planar cells with thin film (~ 5-10 μm) electrolyte membranes will be traced (2,3). Thin film electrolyte technology in planar cell designs has permitted the SOFC to be operated at lower temperatures (600-800 °C) compared to first generation cells operating at 900-1000 °C (5). By contrast, Na/S and Na/NiCl₂ batteries operating at ~ 325 °C have been developed with tubular β "- Al_2O_3 electrolytes due, in part, to higher open-circuit voltages (~ 1.9-2.6 V versus ~ 1 V for the SOFC) and sealing issues related to the containment of liquid electrode reactants (2).

The evolution of β "- Al_2O_3 and zirconia ceramic electrolytes from the time of conception to the fabrication of components with acceptable performance and durability characteristics has taken some 70 years. These electrolytes have been manufactured for use in commercial and prototype electrochemical systems such as chemical sensors, secondary energy storage batteries, fuel cells, thermoelectric power generators, and chemical processing reactors. YSZ electrolytes are also utilized as the ion-conducting phase in composite, two-phase, mixed ionic and electronic conducting electrode systems (6), in the synthesis of sodium-ion conducting β "- Al_2O_3 /YSZ composite electrolytes (7), and as protective coatings for other solid electrolytes.

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