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Editorial

Highly Conductive Ceramics with Multiple Types of Mobile Charge Carriers

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Functional ceramic materials are of interest in many applications due to their structural and chemical richness and the huge range of physical properties that can be generated and modified by the control of the former (electrical conductivity, thermo-mechanical properties, dielectric, piezoelectric, ferroelectric properties, etc.). Crystalline ionic solids exhibit the unique feature of multiple charge carriers, not only electronic carriers (electrons and holes), but also cationic and anionic carriers, both intrinsically, i.e., as pure phase, and extrinsically, i.e., using the effect of dopants. Their contribution depends on 'conduction' mechanisms such as defect formation and interactions, migration paths and barriers, and band structures. This Special Issue focuses on highly conductive ceramics presenting multiple charge carriers. These materials can be classified as mixed electronic and ionic conductors (MIECs) or pure ionic conductors, depending on their respective contributions. The former are studied, for example, as electrode materials for protonic ceramic fuel/electrolysis cells (PCFCs/PCECs) or solid oxide fuel/electrolysis cells (SOFCs/SOECs), while the latter are ideal electrolytes for the same technologies.

1. MIEC

It can be tricky to separate the electronic and ionic contributions when several charge carriers are involved. Pham et al. [1] used the van der Pauw method to determine the conductivity of the cathode composite materials $La_{0.7}Sr_{0.3}MnO_{3\pm\delta}$ (LSM)/$Ce_{0.9}Gd_{0.1}O_{2-\delta}$ (GDC) and $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF)/GDC over a wide temperature range from 800 °C to −73 °C. The samples containing LSM showed reproducible conductivity trajectories, while the LSCF system exhibited unsystematic changes, which may be related to the substantial oxidation/reduction accompanying ferroelastic–paraelastic transitions at 650–750 °C. Combined with structural analysis, they reached the conclusion that a small amount of GDC on the LSCF crystal structures may control the grain size and therefore affect the elastic properties and oxidation/reduction in a subtle way.

Cichy et al. [2] presented the total electrical conductivity of another potential cathode material: the hexagonal rare-earth manganites $Y_{0.95}Pr_{0.05}MnO_{3+\delta}$ and $Y_{0.95}Nd_{0.05}MnO_{3+\delta}$. The results were compared to those of the undoped $YMnO_{3+\delta}$. Despite rather small oxygen content variations (≤0.05), the conduction for $Y_{0.95}Pr_{0.05}MnO_{3+\delta}$ could be improved by three orders of magnitude over $YMnO_{3+\delta}$. The recorded dependences of the Seebeck coefficient on the temperature in different atmospheres for $Y_{0.95}Pr_{0.05}MnO_{3+\delta}$ oxide were found to be complex but generally reflecting the oxygen content variations. The cathodic polarization resistances of $Y_{0.95}Pr_{0.05}MnO_{3+\delta}$ highlighted the enhanced reactivity towards oxygen at lower temperatures in air.

2. Ion Conductors

Na-β″-alumina (Na_2O~$6Al_2O_3$) is known to be an excellent sodium ion conductor, which is used in sodium–sulfur batteries, sodium–nickel chloride batteries, alkali metal thermoelectric converters, and in sensors. Zhu et al. [3] investigated the ion-exchange of Na-β″-alumina + YSZ to form Ag-β″-alumina + YSZ and Li-β″-alumina + YSZ composites. EDS analysis was used to confirm the occurrence of ion exchange. Even though these composites are essentially sodium ion conductors, the oxygen ion conductivity was found to be significant at high temperatures (900 °C). This mixed conduction led to instability of the Ag-β″-alumina + YSZ sample: when heated to 900 °C in air, a thin layer of metallic silver formed on the surface.

The review conducted by Winiarz et al. [4] focuses on protonic ceramic cells, specifically the electrolyte materials (e.g., $Ba(Ce,Zr,Y)O_{3\text{-}d}$) and thin films formed by the pulsed laser deposition (PLD) technique, as well by as using other methods such as RF magnetron sputtering, electron-beam deposition, powder aerosol deposition (PAD), atomic layer deposition (ALD), and spray deposition. Interestingly, the factor that impacts most of the electrical properties of thin films is the film microstructure. The influence of the interface layers, space-charge layers, and strain-modified layers on the total conductivity is also essential but, in many cases, is weaker.

3. Piezoelectric Ceramics

Song et al. [5] characterized the redox behavior, ferroelectric properties, and crystal structure of $Ba_{(1-x)}Sr_xTiO_3$ ceramics. They concluded that the composition with x = 0.30, referred to as BT-30ST, offers significant advantages in high-precision ceramic actuators with an enhanced electrostrictive coefficient Q_{33} = larger than 0.034 m^4/C^2 and an ultra-low hysteresis (<2%) with a high strain (>0.11%).

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