

Oxygen Conductors

Room: Cypress A/B

Session Chairs: Yingge Du, PNNL; Jianhua Tong, Clemson University

10:30 AM

(EAM-ELEC-S5-015-2018) High ionic conductivity at (111) fluorite-bixbyite interfaces (Invited)

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Achieving high ionic conductivity at low temperatures is a key requirement to develop advanced energy conversion and storage devices. Here, we develop a completely new oxide nanobrush architecture with highly enhanced ionic conductivity designed to promote flow of ions perpendicular to the substrate surface. The synthesis technique is capable of growing micron-thick single crystalline fluorite-bixbyite ($\text{CeO}_2\text{-Y}_2\text{O}_3$) nanosuperlattices, in which the (111) interface is engineered to create an interfacial layer with a high density of oxygen vacancies. The resulting ionic conductivity is 1000 times that achieved in bulk CeO_2 with a 30% reduction in the activation energy. The spontaneous formation of the interfacial oxygen vacancies in the $\text{CeO}_2\text{-Y}_2\text{O}_3$ nanosuperlattice is enabled by the artificial charge modulation between Y^{3+} and Ce^{4+} ions generated to cope with the chemical valence mismatch. Our discovery of this fluorite-bixbyite heterostructure provides a new paradigm to develop high-performance ionic nanomaterials, to advance energy and environmental technologies, and to realize oxide nanoionics. *This work was supported by the U.S. Department of Energy, Office of Science, Basic Energy Sciences, Materials Sciences and Engineering Division.

11:00 AM

(EAM-ELEC-S5-016-2018) Influence of Gallium-Based Additives on Microstructure and Ionic Conductivity of Doped-Lanthanum Gallate

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Sr- and Mg-doped lanthanum gallate is a well known oxide-ion conductor with potential application in Solid Oxide Fuel Cells operating at intermediate temperatures (500-700°C). One of the main concerns on this solid electrolyte is related to impurity phases, frequently observed even in chemically synthesized powders, due to gallium loss during sintering. $\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{3-\delta}$ LSGM, containing small amounts of Ga_2O_3 and $\text{Sr}_3\text{Ga}_2\text{O}_6$ were prepared by solid state reaction, and the effects of the additives on microstructure and ionic conductivity were investigated after sintering at 1350°C. Gallium oxide addition promoted grain growth of LSGM and increased the fraction of the gallium-rich impurity phase. In contrast, strontium gallate addition favored reduction of the fraction of impurity phases. The intragrain conductivity of LSGM increases with gallium oxide addition, whereas strontium gallate improved both the intra- and the intergrain conductivities of LSGM.

11:15 AM

(EAM-ELEC-S5-017-2018) On the ionic conduction mechanism in B-Site acceptor doped $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$

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The ferroelectric ceramic $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ (NBT) has been shown to obtain unexpected high oxygen ionic conductivity with Mg B-site and Sr A-site acceptor doping. Initially, a behavior like other regular ferroelectrics was assumed with hardened ferroelectric properties. Therefore, it was quite surprising that Ming Li et al. determined ionic conductivity in the range of good oxygen conductors like yttria stabilized zirconia (YSZ). Hence, new interest in this material

arose in the community investigating oxygen conducting ceramics. Until now there has been no conclusive explanation given for the extraordinarily high and rather complex temperature dependent conductivity. In this work, a possible conduction mechanism is discussed based on results of temperature and Mg concentration dependent impedance data and model calculations including data from a quantum mechanical approach. In the calculations, the defect association and phase dependent changes are taken into account elucidating the mechanism behind the experimentally obtained data.

11:30 AM

(EAM-ELEC-S5-018-2018) p-type electronic conductivity in yttria-stabilised zirconia ceramic electrolytes

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Oxide ion conducting, yttria-stabilised zirconia, YSZ, shows increasing p-type conductivity on application of a small bias at high temperatures, which decreases on removing the bias. This is attributed to redox activity of underbonded oxide ions. Under these conditions, YSZ becomes a mixed conductor in which holes are located on oxygen. In YSZ solid solutions that have high Y content, similar levels of p-type conduction can be introduced simply by increasing the oxygen partial pressure in the surrounding atmosphere. The mechanism by which YSZ becomes a mixed conductor, and the possible consequences for its applications as an electrolyte in solid oxide fuel cells, will be discussed.

11:45 AM

(EAM-ELEC-S5-019-2018) Conductivity Study of B-site Ga^{3+} Doped $\text{Na}_{0.54}\text{Bi}_{0.46}\text{Ti}_{1-x}\text{O}_{3-\delta}$

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Sodium bismuth titanate (NBT) has recently drawn immense research interest because of its high oxide-ion conductivity which is comparable with $\text{Gd}_{0.10}\text{Ce}_{0.90}\text{O}_{2-\delta}$. It undergoes phase transitions from cubic to tetragonal and tetragonal to rhombohedral on cooling below 540-500°C and 400-255°C, respectively. Non-stoichiometric NBT compositions with $\text{Na/Bi}>1$ exhibit at least three orders of magnitude higher conductivity than that of compositions having $\text{Na/Bi}<1$. Recent computational work has predicted that A-site substitution in NBT can render better conductivity than B-site doping. Based on the phase stability study, replacing Na for A-site Bi has been proposed to show high conductivity. Further, considering the factors such as the ionic size, polarizability, and bond strength with oxygen, Ga^{3+} appears to be a suitable dopant in the B-site of NBT for the conductivity enhancement. In the present work, we investigated the influence of Ga^{3+} doping in Na-excess NBT on the phase stability and conductivity. Polycrystalline dense samples of $\text{Na}_{0.54}\text{Bi}_{0.46}\text{Ti}_{1-x}\text{Ga}_x\text{O}_{3-\delta}$ ($x = 0, 1$) were prepared via solid-state reaction method. XRD revealed a single perovskite rhombohedral phase at room temperature. Impedance studies showed 1.5 times increase in total conductivity on 1 mol.% Ga^{3+} doping at 600°C. The conductivity results and the ageing behavior of $\text{Na}_{0.54}\text{Bi}_{0.46}\text{Ti}_{0.99}\text{Ga}_{0.01}\text{O}_{3-\delta}$ at 600°C in air and reducing conditions will be presented.

*Denotes Presenter