IONIC CONDUCTORS

Feel the strain

The high temperatures required for oxygen ion conductivity have hampered the development of practical applications of ionic conductors. Now superlattices made of yttria-stabilized zirconia and strontium titanate show promise for room-temperature devices.

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In 1897, Nernst discovered that he could improve the high-temperature electrical conductivity of oxides by making certain mixtures. He used these mixtures to patent the first practical application of oxygen ion conductors, an incandescent lamp filament which became known as the 'Nernst Glower'. Later the composition of the filament material was simplified to the Nernst mass (85% ZrO_2, 15% Y_2O_3), now known as yttria-stabilized zirconia (YSZ), in which the oxygen ion conductivity is achieved by the oxygen ions migrating by a vacancy mechanism through the cubic fluorite lattice. Since that early start, the continued optimization of oxygen ion conductors has become essential to the development of devices such as the solid oxide fuel cell for clean electrical power generation, and oxygen separation membranes for carbon capture and storage systems. These devices are projected to make vital contributions to the reduction of carbon emissions in the near- and medium-term future, and are the subject of an intense international research effort.

Now J. Santamaria and colleagues[1] have fabricated epitaxial heterostructures formed from a thin layer of YSZ (two unit cells thick) between two much thicker layers of strontium titanate (STO) that increase the conductivity of the YSZ layers by an astonishing eight orders of magnitude (Fig. 1a). They compare the lattice conductivity of single-crystal and thick-film 8 mol% YSZ (bulk) with that of epitaxial trilayer samples in which two 10-nm layers of strontium titanate sandwich a YSZ layer with thickness ranging from 62 nm to 1 nm. When the YSZ thickness is decreased to 30 nm the change is marked, with the conductivity increasing and the temperature dependence (activation energy) decreasing from 1.1 eV to 0.6 eV, giving rise to the remarkable enhancement at low temperatures.

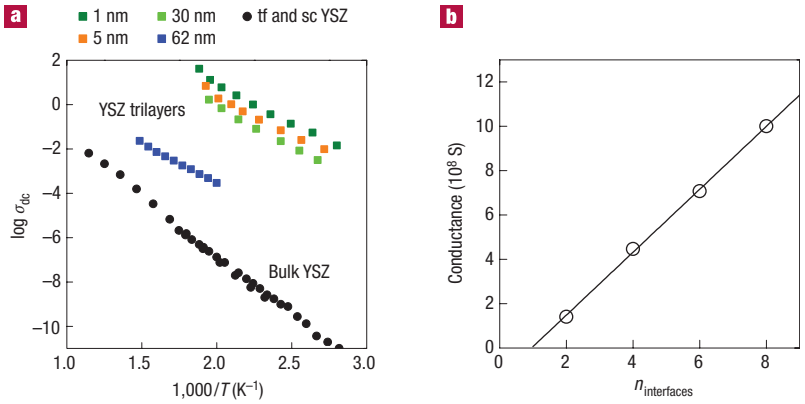

Figure 1 Ionic conductivity of YSZ. **a**, Logarithm of the long-range ionic conductivity (in S cm^{-1}) of the trilayers STO/YSZ/STO versus inverse temperature. The thickness range of the YSZ layer is 1–62 nm. Also included are the data for a single crystal (sc) of YSZ and a thin film (tf), 700 nm thick, with the same nominal composition. **b**, Conductance at 400 K of superlattices consisting of repeated layers of 1-nm YSZ/10-nm STO, as a function of the number of interfaces (the number of [YSZ/STO] repeats is half the number of interfaces). Reprinted with permission from ref. 1. © 2008 AAAS.

Up to now, one of the limiting factors in the development of practical devices based on oxygen ion conductors has been the need for high temperatures to obtain sufficient conductivity. For instance, bulk YSZ achieves usable conductivities (~10^{-1}–10^{-2} S cm^{-1}) at temperatures between 700 and 1,000 °C. This is because the oxygen ion is large and thermal energy is needed to overcome the substantial barriers to its migration into a vacant lattice site. High temperatures of operation in turn lead to durability problems and the use of expensive materials, so one of the main goals of applied research has been the lowering of operating temperatures to around 500–600 °C and perhaps even lower in specialized devices. The huge increase in YSZ conductivity reported by Santamaria and co-workers indicates that substantial conductivities can be achieved close to room temperature.

Enhanced conductivity arising from heterogeneous interfaces has been observed before, stimulated by earlier work[2,3] in which an increase in fluoride ion conductivity seen in CaF_2/BaF_2 superlattice structures of decreasing thickness was ascribed to the layer thickness becoming comparable to the space-charge regions at the interfaces. Work on oxide systems followed, showing that interfacial conductivity of highly textured thin YSZ layers on MgO could be over three orders of magnitude higher than the bulk[4]. Several groups have observed enhancements in thin multilayer oxide systems, with recent reports of a number of systems showing enhancements of varying degrees[5,6], but the conductivity increases observed have been much more modest, one to two orders at most.

The origin of the colossal increase in conductivity in the new system is intriguing. Constructing superlattices consisting of alternating thick STO and thin YSZ layers allowed the dependence on the number of layers to be determined (Fig. 1b). It is clear from the dependences on thickness and the number of layers that the conductivity is due to the YSZ/STO interfaces. The increase in the conductivity accompanied by a decrease in the temperature dependence implies that, at the

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YSZ/STO interfaces, the number of mobile ions increases and they can move much more easily, an effect that those working on bulk properties have sought for many years. Using atomic resolution electron microscopy and energy-loss spectroscopy, the authors identify a modified interface structure (Fig. 2), caused by the epitaxial relationship between the STO and YSZ layers. This leads to a highly disordered oxygen plane at the interface. The epitaxial relationship also imposes a 7% tensile strain on the thin YSZ layer in the plane of the interface. It is suggested that this combination of a large number of mobile ions in the disordered oxygen plane with the opening out of the fluorite lattice of the YSZ induced by the tensile strain leads to the high interfacial conductivity. A recent report from one member of the team (http://ceramictechweekly.org/?p=369) has indicated that this strained structure is apparent from high-resolution electron microscopy of the structure.

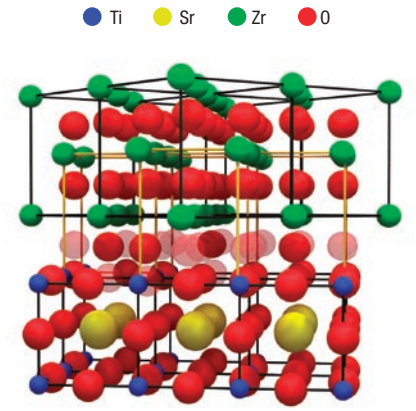

Figure 2 Solid-spheres model of the YSZ/STO interface showing a three-dimensional view of the interface. The shaded oxygen atoms represent the empty positions available for oxygen ions at the interface. To make it easier to visualize the oxygen vacancies at the interface, ionic radii are not to scale. Reprinted with permission from ref. 1. © 2008 AAAS.

These remarkable results clearly need to be repeated and verified by other groups working with oxygen ion conductors, and crucially, the charge carrier needs to be confirmed as the oxygen ion. Nevertheless, the indications from this and other work[4–6] are that the enhancement effect is substantial. The implications of this finding could have a profound effect on the current use of oxygen ion conductors in clean energy applications and, as the authors themselves point out, could lead to exciting new technologies based on nanostructured low-temperature oxygen ion conductors.

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DIELECTRIC MATERIALS

Gels excel

Printing electronic circuits will usher in a new era in electronics. With ion gel dielectrics, unprecedented transistor performance and speeds at low voltage can be demonstrated.

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The next wave in the microelectronics revolution may arise in the form of flexible circuitry, sensors and displays printed on the surfaces of a host of everyday items such as magazine covers, wine bottles and clothing[1]. Indeed, some of these things are already happening. Perhaps surprisingly, the commercial graphics and printing industry has been the main driver for the emergence of flexible electronics. Industries worldwide see potentially exciting opportunities in printing 'functional inks' to make the maze of circuitry required for flexible radiofrequency identity tags, smart labels, simple displays and disposable sensors[2]. Retailers forecast maximum efficiency and reduction of inventory costs, and consumers will benefit from efficient product information, such as item history in the food supply chain.

The building block of every electronic circuit is the thin-film transistor, which is composed of three fundamental materials: the semiconductor, dielectric and conductor (Fig. 1)[3]. Flexible electronics requires the printing of all of these materials. The bottleneck of this technology is the development of materials that can be solution-processed and formulated into 'electronic inks'. After printing, the resulting dried layers must show good electrical properties[4,5]. Although most of the emphasis has been placed on developing new semiconductors, a great concern in this field is the performance of printable dielectrics[6]. Dielectrics are electronic insulators (typically plastic or glass) used in capacitors to store charge and also in transistors to allow carrier accumulation in the semiconductor. One of the figures of merit for dielectrics is their specific capacitance, or the amount of charge per unit area that they can accommodate in a capacitor. In general terms, the capacitor and transistor performance improve with higher specific capacitance; they can store more charge and switch larger currents at lower voltages if the specific capacitance is high. The problem has been to find printable dielectrics with high specific capacitance. On page 900 of this issue[7], the group led by Daniel Frisbie and Timothy Lodge at the University of Minnesota demonstrate a creative solution to this problem using 'ion gel' inks that are ionic conductors, but electronic insulators.

Ion gels are an interesting class of materials in their own right. They comprise a room-temperature ionic liquid and, in the case of the work by Frisbie *et al.*, a self-assembling triblock copolymer that creates a rubbery network that is infused with the ionic liquid. Ionic liquids are organic salts molten at room temperature; they have negligible vapour pressure and are highly ionically conducting because each molecule in the liquid is a mobile ion[8]. The purpose of adding the triblock copolymer is to add mechanical integrity to the ionic liquid so that after printing from a solvent, the solvent-dried ion gel does not flow.

From a flexible electronics perspective, the key point is that ion gels are both printable and have tremendous specific capacitances, in excess of 10 μF cm^{-2},

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