Materials design of solid electrolytes

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Solid electrolytes play an important role in several technological applications, such as fuel cells. Optimization of such materials is often done by trial and error. The work of Andersson *et al.* (1) in this issue of PNAS demonstrates that the choice of dopants can be guided by computer simulations, in which parameters that are essential for the high ionic conductivity are determined from a series of first-principles density functional theory (DFT) calculations (2). The material of interest is ceria (CeO_2), which can be doped to optimize the ionic conductivity. The parent compound has a simple cubic structure (Fig. 1), in which the Ce ions form a face-centered-cubic (fcc) structure and the oxygen ions form a simple cubic sublattice. The current flows by means of oxygen ions, which are transported through the lattice in a vacancy-assisted activated process. Vacancies occur, for example, when ceria is doped with lower valence cations, but interactions between dopants and vacancies often prevent the vacancies from being mobile. The authors make

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the exciting observation that, in an optimal case, the interactions, which are caused by the dopants, can and should be balanced between repulsive elastic and attractive electronic parts.

Although ceria has a rather simple crystal structure, the doped ceria system looks hopeless because it is disordered, contains trivalent cations from the lanthanide series with *f* electrons, and has various dopant site preferences and rather small energy differences corresponding to vacancy formation, association, or migration. Nevertheless, modern DFT calculations allow us to solve these problems by modeling doped ceria with a supercell approach, in which various

Fig. 1. The crystal structure of doped ceria. In the right cube, the undoped CeO_2 is shown, whereas in the left cube, two of the cerium ions are replaced by trivalent ions from the lanthanide series (dark spheres), between which an oxygen vacancy appears (indicated by a small sphere).

ordered impurity and defect structures can be studied. With the increased computer power that is available nowadays, the size of the supercell can be made sufficiently large to avoid effects from the assumed order or periodic images, which are caused by the artificial translational symmetry. The volume of the supercell is not crucial, whereas the relaxation of the internal structural parameters around a dopant is important to minimize the energy of each structure, which represents a possible vacancy–dopant configuration. To find the most stable or likely configuration, high precision is needed that was lacking in the past. Many of the calculated properties, in particular the energies, show a clear trend across the lanthanide series, often with a crossover near Pm^{3+} . This ion is not a good candidate for doping because of its radioactivity, but a combination of dopants can lead to an average atomic number in this range. Computer simulations, including systems that do not exist, can provide physical insight, from which a search of optimal materials can be done systematically instead of by trial and error.

Perhaps the most important lesson to be learned from the work of Andersson *et al.* (1) is that the activation energy for oxygen vacancy diffusion has a clear minimum in the lanthanide series. Materials with a lower activation energy will have sufficient ionic conductivity at

lower temperature, which is important for technological applications. Although DFT simulations may not be perfect for a single system, they can well reproduce trends and provide a physical picture, from which one can make an educated guess for optimization of materials. The systematic study of the whole lanthanide series was computer-intensive work but provided the basis for finding trends. In the present case, the use of relatively large supercells was important for the quality of the simulation, because the treatment of lattice relaxations around dopant sites, oxygen diffusion, or site preferences of vacancies all require a long distance in between to avoid effects from the periodic images. Such DFT calculations have reached nearly chemical accuracy because of the improvement of both the functionals used in DFT and the method of calculation to solve the Kohn–Sham equations. This article is a striking example of how effective DFT simulations have become in atomistic materials science. In combination with the ever-increasing computer power, improved functionals and methods of solution have made DFT calculations nearly as reliable as chemical experiments.

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