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Composites of Ceramic High-Temperature Proton Conductors with Inorganic Compounds

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This work deals with composites of high-temperature proton conductors and inorganic compounds such as carbonates, hydroxides, and chlorides. Discontinuities were found in the σT *vs.* $1/T$ plots which are ascribed to superionic phase transitions occurring in the interface region between the constituent phases. A similar superionic phase transition was also found between a composite of a proton conductor and a prominent oxygen ion conductor. The results provide a natural explanation for the high conductivities recently reported for similar composites of oxygen ion conductors and such inorganic compounds [B. Zhu, *J. Power Sources*, **114**, 1 (2003)] and also explains the high current densities obtained in intermediate temperature fuel cells based on such composites.
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Ceramic high-temperature proton conductors (HTPCs) are often perovskites which are suitably doped to contain oxygen vacancies. Typical examples are the compounds $BaCe_{0.9}Y_{0.1}O_{2.95}$ (BCY10) and $BaCe_{0.8}Y_{0.2}O_{2.9}$ (BCY20). These react with water according to[1]

$$(H_2O)_{gas} + V_O^{\bullet\bullet} + O_O^{\times} \Leftrightarrow 2OH_O^{\bullet}$$

In this way protonic defects are introduced. If the conductivity due to these defects is much larger than the one caused by other defects we have a HTPC. However, there are limits to the proton conductivity increase by such homogeneous or (aliovalent) doping. Higher levels of proton conductivity may, in principle, be achieved by heterogeneous doping, or composite formation.[2] Composites are basically physical mixtures of two phases with little or no chemical interaction between them. In the case of composites of HTPCs, or heterogeneous doping of HTPCs, there are two possibilities: the insertion of second phase particles into a HTPC matrix and/or the production of a matrix of the second phase in which you disperse fine HTPC particles.

An example of this second case is the work of Bin Zhu and colleagues,[3] where essentially a matrix of a 'salt' (the inorganic compound) is formed, often by melting, in which fine powder of a good oxygen ion conductor (*e.g.*, $Ce_{0.8}Gd_{0.2}O_{1.9}$) is dispersed. In Ref. 3, very high current densities at intermediate temperatures are claimed for fuel cells built with such composites as electrolytes and electrodes. To the best of our knowledge there are no studies on composites of HTPCs with inorganic compounds. A special exception is recent work on composites of oxygen ion conductors and HTPCs[4] without further inactive phases. There are a number of studies, however, on low and medium temperature proton conductors where a dramatic increase of proton conductivity with heterogeneous doping was demonstrated.[5,6]

We study here composite systems of a HTPC plus an inorganic phase exhibiting high conductivities. A few cursory experiments on composites of the oxygen ion conductor $Ce_{0.8}Gd_{0.2}O_{1.9}$ are also included. One of the main goals of this study is to understand the reason for the high conductivities in the composite work of Bin Zhu *et al.*[3]

Experimental

In brief, BCY20 powder was prepared by sol-gel techniques,[7] BCY15 and BCY10 using the mixed oxide route. The powders were milled to ~0.5 μm particle size. After mixing, the HTPC with the inorganic compound, usually 20 wt %, planetary milling was used again for homogenization and particle size reduction. Hot pressing between 450 and 700°C was employed. Altenatively, pellets were first pressed uniaxially, followed by cold isostatic pressing and annealing at 500 to 700°C. Ag paste was used for the outer electrodes. Impedances were determined with a Solartron 1260 unit. Humid air was produced by bubbling air through water at ambient temperature ($p_{H2O} \cong 30$ mbar).

Results

Figure 1 shows the conductivity plot of a BCY20-20 wt % Li_2CO_3-Na_2CO_3 (2:1) composite. A sharp discontinuity is seen at ~400°C. Above that temperature there is a very high conductivity. The slope of 0.55 eV in the high-temperature branch is indicative of proton conduction.[1] No significant differences are observable between dry and moist conditions. The discontinuity in the σT *vs.* $1/T$ plot is interpreted here as a superionic/superprotonic phase transition in the boundary phase formed between the constituent phases. We have observed similar σT discontinuities in the following systems; the transition temperature is given in parentheses: Y-doped Ba cerate with Li_2CO_3 alone (520°C), Y-doped Ba cerate with NaOH (440°C), and Y-doped Ba cerate with LiCl (440°C).

The σT *vs.* $1/T$ plots of these composites look very much like the one in Fig. 1. All of these transitions are also viewed as superionic/superprotonic phase transitions.

Cursory results involving the oxygen ion conductor $Ce_{0.8}Gd_{0.2}O_{1.9}$ demonstrate that the σT *vs.* $1/T$ curves of a $Ce_{0.8}Gd_{0.2}$ $O_{1.9}$-[Li_2CO_3 + Na_2CO_3-20 wt % (2:1)] composite also display a pronounced discontinuity, this superionic phase transition occurs here near 550°C. The impedance of a BCY15 (25%) + $Ce_{0.8}Gd_{0.2}O_{1.9}$ (75%) composite was also studied in view of our previous study on a composite of BCY20 + $Ce_{0.8}Sm_{0.2}O_{1.9}$[4] which is similar in composition. Not unexpectedly, we also observe in this circumstance a σT discontinuity or superionic phase transition.

However, there were also negative results with no σT discontinuities. No superionic phase transitions or enhanced conductivities were observed in the following systems: BCY20 + $BaCO_3$, BCY20 + $BaSO_4$, BCY20 + nano ZrO_2, BCY20 + Al_2O_3 (Al_2O_3 is the classical compound for heterogeneous doping), and BCY20 + CaF_2 + BaF_2

Discussion

According to Maier[2] there are highly conducting parallel contributions due to space charge zones near phase boundaries. The defect concentrations are much higher in these space charge zones than in the bulk. For small dimensions the zones may even overlap leading to an enhanced conductivity. Also, the Brouwer diagrams are different for the space charge zones.[2]

On the other hand, there is the aspect of disordering phenomena in superionic conductors; for a recent review see Ref. 8. It is very plausible that the present superionic transitions are confined to the interface regions. Here, the defect density is so elevated that the structure may change to a superionic one when a certain critical temperature is exceeded. Normally, superionic conductors tend to involve small cations such as H^+, Li^+, Cu^+, and Ag^+. But there is

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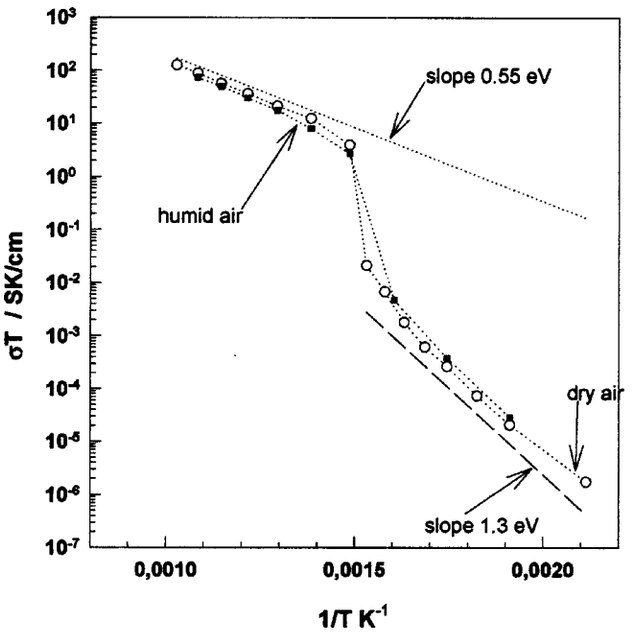

Figure 1. Impedance of a composite of: BCY20 + 20 wt % Li_2CO_3 + Na_2CO_3 (2:1), measured in dry and moist air, Ag electrodes. Note superionic/protonic phase transition and different slopes.

also a contribution from larger anions such as F^- and O^{2-}.[8] Typical activation energies are ~0.5 eV for H^+ and, in fact, similar energies were found in our experiments.

One might argue that we merely observed conductivity increases due to melting. However, in only one of the present transitions (Y-doped Ba cerate with NaOH (440°C.)) does the discontinuity occur above the melting point of the inorganic phase, here NaOH, which melts at 323°C. In all other cases, the nominal melting point of the inorganic compound is above the observed transition temperature. Conceivably, the newly formed phase between the two constituent phases could have its melting point at the transition. But then it is the essence of a superionic phase transition that melting of one species on a sublattice occurs at the critical temperature.

Obviously, the present results present no proof of superionic transitions occurring in the interfacial regions or phases, but they are a strong indication of such events. Proof can only be obtained from scattering or diffraction experiments. These may not be trivial, as the boundary phase volume presumably is small.

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