Materials with three mobile carriers (oxygen vacancies, protons, holes) are of interest as cathode materials for proton-conducting ceramic fuel cells. The incorporation of protons into such mixed-conducting oxides can occur by acid-base hydration of oxygen vacancies as well as by hydrogen uptake.[1,2] Depending on conditions, one-fold or two-fold conductivity relaxation after pH\textsubscript{2}O steps is observed.[2-6] Exact analytical relations for these processes were derived in ref. [2]. For a complete description four diffusion coefficients are required, comprising direct as well as "indirect" terms. The complex non-monotonic kinetic behavior is related to the fact that in a three carrier system the electroneutrality condition does not lead to a simple coupling between the carrier fluxes. Numerical simulations for a wide range of materials and conditions are presented.[2,6] They allow us to identify the conditions for the transition from one-fold to two-fold relaxation, and give a natural explanation for the "moving boundary phenomenon" observed in ref. [3].

The simulations also show that the assignment of the temperature dependence of the effective diffusivities for acceptor-doped (Ba,Sr)(Zr,Ce)O\textsubscript{3-δ} perovskites (large set of experimental data compiled in [7]) is far from trivial. When the transference number of oxygen vacancies exceeds that of the protons, the faster of the two effective diffusivities approaches the oxygen chemical diffusion coefficient, not the hydrogen chemical diffusivity as one might expect intuitively. Furthermore, the effect of trapping reactions on the relaxation kinetics is investigated.