In this contribution, I provide a comprehensive picture of the potential energy landscape for oxygen-vacancy migration in the lattice of ceria-based solid electrolytes based on the results from a combined application nuclear magnetic resonance and electrochemical impedance spectroscopy. The oxygen vacancies in acceptor-doped ceria perform rapid symmetry-related jumps in the nearest-neighbor coordination shell of the dopant traps as well as hopping from one trap to another over length scales of a few nanometers. The hopping of vacancies between the dopant traps control the ionic conduction process in the ceria solid solutions. In addition, I discuss the extra potential barrier forms at the grain boundary in polycrystalline ceria electrolytes. The additional barrier attributed to the formation of the space charge in the vicinity of the grain boundary results in substantial current obstruction across the grain boundary. It is the high grain boundary resistance that reduces the effective conductivity in ceria-based solid electrolytes. The potential barrier height has been determined using the ratio of the grain boundary resistivity to the bulk counterpart exclusively to date. I will demonstrate using a simple consistency check that the resistivity ratio overestimates the barrier height. Finally, I introduce a new linear diffusion model which allows for more accurate determination of the potential