The thermal evolution of the phase composition of CeP2O7 and Ce(PO3)4 with 10 mol% Y and Gd doping, respectively, was examined by in-situ powder X-ray diffraction and thermogravimetry with in-line mass spectroscopy. The phase composition depends critically on the P to metal ratio, the annealing temperature, humidity and time. CeP2O7 and Ce(PO3)4 were completely decomposed to CePO4 following a 1100 h long conductivity test at 155°C. The conductivity of 10 mol% Gd doped Ce(PO3)4 (synthesized with P: (Ce + Gd) = 5.0) reaches a value of 6.4·10⁻² S·cm⁻¹ at 150°C under wet conditions (pH₂O = 0.2 atm). The conductivity of 10 mol% Y doped CeP2O7 (synthesized with P: (Ce + Y) = 3.1) was 1.9·10⁻² S·cm⁻¹ under the same conditions. Long term conductivity measurements are reported here for the first time and the effect of repeated hydration-dehydration cycles on the conductivity is examined. Exsolution of PmOn and increase of the highly hygroscopic amorphous secondary phase significantly affects the conducting properties. KH₂PO₄ was observed to re-crystallize and form amorphous potassium phosphate at temperatures above 100°C in the 10 mol% Y doped CeP2O7:KH₂PO₄ composite (synthesized with P: (Ce + Y) = 3.1) resulting in a conductivity value of 2.6·10⁻² S·cm⁻¹ at 150°C and pH₂O = 0.2 atm.