CATHODE MATERIALS FOR PROTONIC CERAMIC FUEL CELLS: BULK DEFECT CHEMISTRY AND SURFACE REACTION KINETICS

Rotraut Merkle, MPI for Solid State Research, Stuttgart, Germany
r.merkle@fkf.mpg.de

Key Words: Protonic ceramic fuel cell, surface reaction kinetics, defect chemistry, microcontact impedance

Fuel cells based on ceramic proton conductors receive growing interest because these electrolytes offer a higher ionic conductivity compared to oxide ion conductors, in particular at 300-600 °C. To extend the oxygen reduction reaction to water beyond the three-phase boundary, cathode materials for such cells should have a certain proton conductivity. Since the perovskites considered as cathode material exhibit perceptible oxygen vacancy, proton and hole concentrations, proton uptake can occur by water incorporation (acid-base reaction) and by hydrogen incorporation (redox reaction) [1]. The presence of three mobile carriers can lead to a complex two-fold stoichiometry relaxation kinetics, requiring four diffusion coefficients for complete description [1,2].

The different regimes of proton uptake are explored by thermogravimetry (pH_2O changes in different pO_2) for perovskites such as $La_{0.5}Sr_{0.5}FeO_{3-\square}$ and $Ba_{0.5}Sr_{0.2}Fe_{0.8}Zn_{0.2}O_{3-\square}$ (BSFZ). The obtained maximum proton concentrations are significantly lower than in $BaZrO_3$ electrolyte materials at same T and pH_2O [3]. The proton mobility in BSFZ extracted from the transient behavior is comparable to that in $BaZrO_3$ electrolytes. Correlations between cation composition and amount of incorporated protons are discussed.

The kinetics of oxygen reduction to water is measured by impedance spectroscopy at dense thin-film BSFZ microelectrodes on proton-conducting $Ba(Zr,Y)O_3$ as substrate. The dependence of surface reaction resistance on electrode area demonstrates that the proton conductivity of BSFZ in the range of $\approx$ 10^{-3} S/cm at 400 °C [4] indeed suffices to transport protons from the $Ba(Zr,Y)O_{3-\square}$ electrolyte through the dense BSFZ film to the gas interface. The reduction of O_2 to water can in principle proceed without oxygen incorporation into the cathode material. The values of the pO_2 and pH_2O dependence of the effective rate constant indicate that molecular oxygen species participate in the rate determining step, and that protonated oxygen species appear only after this step [5].

[1] D. Poetzsch, R. Merkle, J. Maier, Adv. Funct. Mater. 25 (2015) 1542
[2] R. Merkle, R. Zohourian, J. MAier, Solid State Ionics (2016) doi:10.1016/j.ssi.2015.12.011
[3] D. Poetzsch, R. Merkle, J. Maier, Farad. Disc. 182 (2015) 129
[4] R. Merkle, D. Poetzsch, J. Maier,ECS Transact, 66(2) (2015) 95
[5] D. Poetzsch, R. Merkle, J. Maier, J. Electrochem. Soc. 162 (2015) F939