Isotope Exchange Depth Profiling and Quantum Simulation Studies of Irradiated Yttria Stabilized Zirconia

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Yttria Stabilized Zirconia (YSZ) is used as a solid electrolyte for SOFCs due to its high oxygen-ion conductivity. At present, however, practical applications for SOFCs are by the high operating temperatures that are needed to create the necessary level of vacancy mobility. To increase ionic conductivity for low temperature applications, we report an approach that involves dilating the structure by irradiation and introducing edge dislocations into the electrolyte.

In this study, single crystal YSZ samples are irradiated by 300 keV Xe^{3+} at a dose of 10^{15}-10^{16} ions/cm^2. With this high dose of heavy ion irradiation, point and line defects are introduced into the material. During heat treatment that follows irradiation, the dislocation loops interact and form complex dislocation networks. Isotope exchange depth profiling (IEDP) experiments were performed to verify enhanced ionic diffusivity and surface exchange properties.

Isotope exchange experiments involved evacuation of the vessel to at least 10^{-6} torr followed by the introduction of research grade $^{16}O_2$. The irradiated and non-irradiated (control) samples were annealed in the same ampoule in $^{16}O_2$ environment for at least six times the exchange time at selected temperature. During rapid cooling to temperatures below 150 °C, the apparatus is evacuated to 10^{-6} torr. The labeled $^{18}O_2$ was sequentially introduced into the vessel. The exchange was then performed at selected temperatures.

Following the isotope exchange, the penetration profiles of the isotope were analyzed by Secondary Ion Mass Spectrometry (SIMS) equipped with quadrupole mass analyzer, and using 5 keV $^{133}Cs^+$ primary ions impacting the surface of the samples at an ion flux of 100 nA. The depth profiles were sequentially obtained by collecting secondary ion counts as a function of time. Afterward, the corresponding crater depth was measured and the profiles were presented as a function of depth (Figure 1).

To extract the diffusion coefficient of the tracer oxygen ion, the solutions to Fick's second law in 1-D semi-infinite medium were used with least square fit of the profiles for the non-irradiated samples, while a semi-infinite two-region medium was employed for the irradiated samples [1]. The preliminary results from IEDP technique on non-irradiated and irradiated YSZ single crystal (100) surface reveal the enhancement of the oxygen diffusivity at the irradiated region (Figure 2). The activation energy for oxygen tracer diffusion in the irradiated region is 0.6 eV, which is lower compared with 1.06 eV in the single crystal region. Based on these promising results, we will repeat these experiments for (110) and (111) YSZ surfaces also.

To gain insight into the diffusion mechanism, quantum simulation using Density Functional Theory (DFT) complemented with Kinetic Monte Carlo (KMC) techniques was employed. The Projector Augmented Wave (PAW) pseudopotential based on Local Density Functional Theory was used to calculate the diffusion barrier height at different yttrium arrangements

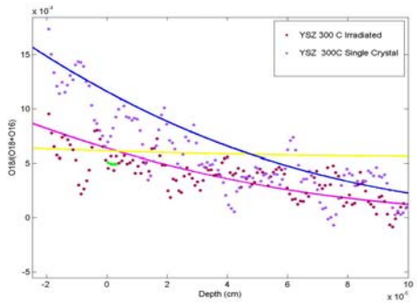

Figure 1. SIMS depth profile of irradiated and non-irradiated YSZ single crystals annealed at 300 °C for 30 minutes

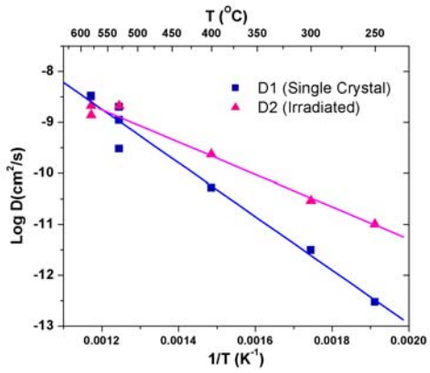

Figure 2. Arrhenius plot of oxygen self-diffusion in irradiated and non-irradiated YSZ single crystals

surrounding diffusing oxygen ions and oxygen vacancies. Cubic YSZ supercells with periodic boundary conditions were used in the calculations. The preliminary results reveal the diffusion barrier in YSZ varies from 0.2 eV to 1.4 eV depending on the relative positions of surrounding vacancies and Y atoms.

KMC was then used to simulate random walk process in a randomly distributed landscape of vacancy and Y atoms. KMC was also used to approximate the diffusion coefficient and extract the activation energy of the simulated diffusion process. Preliminary results replicated the experimental results which showed highest diffusivity around 8-10 mol% YSZ. We are currently exploring this method to study diffusion along the dislocation core in YSZ.

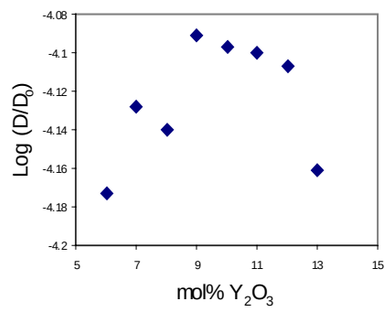

Figure 3. Estimated diffusion coefficient of oxygen ion in different concentrations of Y_2O_3 at 1100 K calculated by KMC method

Reference:
[1] M. de Ridder, et al. Solid State Ionics 158 (2003) 67-77