LOCAL STRUCTURAL ANALYSIS ON HYDRATION BEHAVIOR IN DOPED AZrO$_3$ (A = Ba, Ca) PROTONIC CONDUCTORS

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Perovskite-type protonic conductors are candidate electrolytes for intermediate temperature solid oxide fuel cells. For practical application, further improvement in proton conductivity is needed. Proton migration in these materials has been reported to be limited by trapping effects of protons by acceptor dopants [1]. In addition, it is suggested that the formation of percolation path with the trapped protons can lower the activation barrier for long-range proton migration and result in enhancement of proton conductivity. The formation of this percolation path is dominated by the location of protons and their concentrations, and higher proton concentration than the percolation limit is necessary for long range transport of protons. To increase or control the proton concentration in the material, understanding of hydration behavior is important because protons are incorporated into the material via hydration reaction of water vapor and oxygen vacancies. Therefore, this study focuses on investigation of hydration behavior from the local structural viewpoint with respect to protons and oxygen vacancies to explore a strategy to improve proton conductivity. For this purpose, solid-state nuclear magnetic resonance combined with density functional theory (DFT) calculations is used to elucidate the local structure of protons and oxygen vacancies since this technique is sensitive to the difference in chemical environment of probing nuclei. In the previous study base on ^{45}Sc NMR analysis, difference in the local structure around oxygen vacancies in Sc-doped AZrO$_3$ (A = Ba, Ca) is suggested to be related to the hydration behavior [2]. To clarify the influence of the local structure around oxygen vacancies to the hydration behavior, the electric-field gradient (EFG) at Sc sites, an indicator of the local structure, in Sc-doped AZrO$_3$ is calculated by DFT calculation and compared with ^{45}Sc NMR results. EFG at Sc sites is derived from the charge of oxide ions surrounding the nucleus. When the symmetry of the surrounding oxide ions is lowered due to the formation of the oxygen vacancy, large gradient in the electric-field at the Sc site is generated. This EFG interacts with the electric quadrupole moment of Sc nucleus, and this interaction can be observed by ^{45}Sc NMR.

Figure 1 shows the EFG at Sc sites, represented as the quadrupole coupling constant C_Q, obtained from DFT calculation and ^{45}Sc NMR results for Sc-doped BaZrO$_3$ and CaZrO$_3$. C_Q of two different 5-coordinated Sc is calculated in the case of CaZrO$_3$ because CaZrO$_3$ has two crystallographically different oxide ion sites. The C_Q of Sc sites in Ba-Sc oxides is also calculated and shown as a reference. All the reference oxides have 6-coordinated Sc, and their C_Q shows good agreement with the NMR results. In the case of 5-coordinated Sc in BaZrO$_3$ and CaZrO$_3$, C_Q from DFT calculation tends to show larger value compared to the NMR results. However, the trend agrees with the NMR results. In the NMR results, BaZrO$_3$ shows larger C_Q compared to CaZrO$_3$ which indicates lower symmetry of 5-coordinated polyhedra of Sc in BaZrO$_3$. By analyzing the difference in the symmetry of 5-coordinated polyhedra based on the DFT results, the large C_Q of BaZrO$_3$ seems to be originated from the large displacement of oxide ions due to the formation of the oxygen vacancy. From thermogravimetric analysis, Sc-doped BaZrO$_3$ incorporates more than 10 times larger amounts of proton than CaZrO$_3$. These results indicate that hydration in these materials occurs to relax the local structure around the oxygen vacancy with large displacement of oxide ions by filling the vacancy with the hydroxide ion.

Figure 1 Quadrupole coupling constant, C_Q, of Sc sites obtained from DFT calculation and ^{45}Sc NMR measurements

References
[1] Y. Yamazaki et al., Nat. Mater. 12 (2013) 647-651.
[2] I. Oikawa et al., Solid State Ionics 213 (2012) 14-17.