Applications of X-ray Absorption Spectroscopy in Structural Characterization of Rare-earth Metal Oxides

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Pr-doped ceria-based oxides with $Ce_{1-X}Pr_xO_{2-\delta}$ (x = 0.05-0.4) formula and abbreviated as xCPO were synthesized by Pechini process, and the pressed pellets were sintered at 1500 °C in air in order to apply as the solid electrolyte in solid oxide fuel cell. The valencies of Pr in ceria were investigated by X-ray absorption near-edge spectroscopy (XANES) at beam line 17C of NSRRC and a mixed valences of +3 and +4 was found.

The number of oxygen vacancy in ceria increases when more Ce^{4+} in ceria are substituted by lower valence cations, such as Gd^{3+}, Y^{3+}, and Sm^{3+}…etc. and that is one of important factors affecting the conductivity of ceria-based electrolyte. In the present study, Pr^{3+} was chosen as the doped cation to substitute Ce^{4+} in ceria. Pr-doped ceria (xCPO) of the formula $Ce_{1-x}Pr_xO_{2-\delta}$ where x=0.05-0.35 was prepared by Pechini process and were used as the electrolytes in ITSOFC. All the doped materials were ceria based solid solution of fluorite type structure, characterized by X-ray powder diffraction. The ionic conductivities of these electrolytes were measured at 400-800 °C in air by using AC impedance spectroscopy. Among the doped material, $Ce_{0.7}Pr_{0.3}O_{2-\delta}$ (30CPO) was found to have the highest conductivity of 0.0668 Scm^{-1}.

The valencies of Pr doped in ceria compounds were investigated by X-ray absorption near-edge spectroscopy (XANES) at beam line 17C of NSRRC and the Pr L_{III}-edge XANES spectra are showed in Figure 1. The spectra of Pr_6O_{11} and Pr_2O_3 were used as the standard, since compounds of pure Pr^{4+} were not available. The spectrum of Pr_6O_{11} shows two peaks at 5969 and 5979 eV, while that of Pr_2O_3 shows mainly a strong peak at 5968 eV. Since the atomic ratio of Pr^{3+}: Pr^{4+} in Pr_6O_{11} is 1:2, the stronger peak at 5969 eV and the weaker peak at 5979 eV cannot be simply assigned to Pr^{3+} and Pr^{4+}, respectively. However, a qualitative assignment can be made by saying that Pr^{4+} is present if the 5979 eV peak appears.

For the $Ce_{1-X}Pr_xO_{2-\delta}$ compounds, similar features as that of Pr_6O_{11} were observed in all spectra except 10CPO. These results imply that a portion of Pr^{3+} ions doped in ceria was oxidized to Pr^{4+} in the sintering process. As a result, much lower number of oxygen vacancies was created in the sample than would be expected from the original doping ratio.

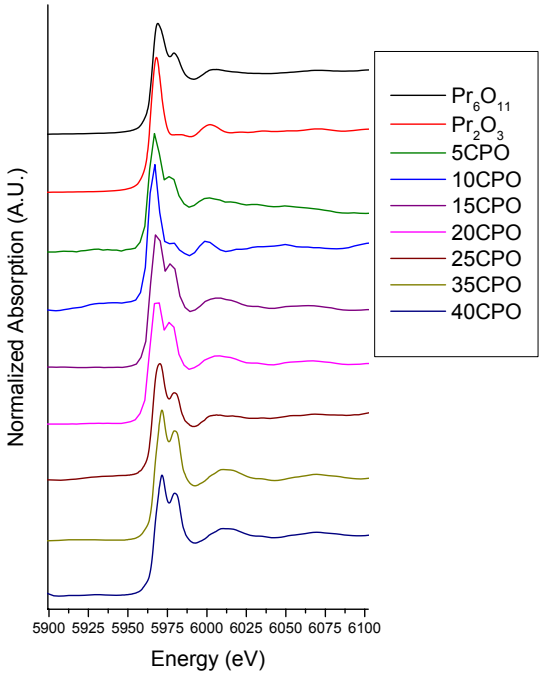

Figure 1. Pr L_{III}-edge XANES spectra of Pr-containing oxides.