

## PREPARATION OF RARE EARTH OXYFLUORIDES AND THEIR PROPERTIES AS A MATERIAL FOR FUEL CELL

Masayuki Takashima\* and Gentaro Kanoh

Department of Industrial Chemistry, Fukui University, 3-Bunkyo, Fukui 910 (Japan)

The formation of rare earth oxyfluorides and their properties as an electrocatalyst and/or a solid electrolyte using for fuel cell were studied by means of x-ray and electrochemical methods.

By a high temperature solid reaction between rare earth fluorides and rare earth or zirconium oxides not only the simple oxyfluoride such as NdOF, SmOF, CeOF and YOF but also the binary one written by  $Nd_{1-x}Ln_xOF$ ,  $(NdOF)_{1-x}(MO)_x$  and  $(ZrO_2)_{1-x}(LnF_3)_x$  were obtained, where Ln; Y, La, Nd, Sm and Yb, MO; alkaline earth oxide and Nb<sub>2</sub>O<sub>5</sub>. On the solid reaction process, it was found that the exchange reaction of anion, that is F<sup>-</sup> and O<sup>2-</sup>, took place at first between the rare earth fluoride and the oxide. LnF<sub>3</sub> could form the solid solution with ZrO<sub>2</sub> at above 1200 °C taking the fluorite structure in the composition range of below 30 mol%-LnF<sub>3</sub>, so-called the stabilized zirconia.

The crystal type of these oxyfluorides was any one of the rhombohedral, the cubic and the tetragonal. The cubic phase oxyfluorides contained Nd showed high electrocatalytic activity for both the hydrogen oxidation and the oxygen reduction. Then (NdOF)<sub>0.9</sub>(Nb<sub>2</sub>O<sub>5</sub>)<sub>0.1</sub> and (ZrO<sub>2</sub>)<sub>1-x</sub>(LnF<sub>3</sub>)<sub>x</sub> were found to act as the oxide ion conducting solid electrolyte.

## USE OF FLUORINE IN THE PHENOMENONS CONNECTED WITH THE FLUOROPOLYTUNGSTATES REDUCTION

F. Chauveau\*, P. Doppelt and J. Lefebvre

Laboratoire de Chimie des Polymères Inorganiques – Université Pierre et Marie Curie, 8 rue Cuvier, 75230 Paris, Cedex 05 (France)

If a variable number of fluorine atoms is introduced in the metatungstate ion,  $[H_2W_{12}O_{40}]^{6-}$ , new varieties of heteropolyanions of the types:  $[HW_{12}FO_{39}]^{6-}$ ,  $[H_2W_{12}FO_{39}]^{5-}$ ,  $[HW_{12}F_2O_{38}]^{5-}$ ,  $[H_2W_{12}F_2O_{38}]^{4-}$  and  $[HW_{12}F_3O_{37}]^{4-}$  are formed. Fluorine, thus replacing oxygen can be used as a probe in order to solve problems arising during the electrochemical reduction of heteropolyanions.

The reduction at a controlled potential leads to a great number of mixed valency compounds, formed as brown coloured derivatives, which correspond to the fixation of 6, 12, 18 and 24 electrons per mole. It has been proven by fluorine NMR that in the initial compounds the fluorine atoms were concentrated in the central tetrahedron of the very compact structure. This feature is found again in the reduced series and fluorine NMR is also used to explain the structure of the later ones. This way, we can check the hypothesis by which in this polyanion type one new brown series appears through fixation of 6 electrons, these later are located on a tritungstic group forming a real cluster  $W_3O_{12}(F)$  in the polyanion.