# Laboratory of Inorganic Materials Chemistry

Professor: Nobuhito Imanaka, Associate Professor: Toshiyuki Masui,

Assistant Professor: Shinji Tamura

URL: http://www.chem.eng.osaka-u.ac.jp/~imaken/

E-mail: imanaka@chem.eng.osaka-u.ac.jp



## High-Valent Cation Conducting Solid Electrolytes

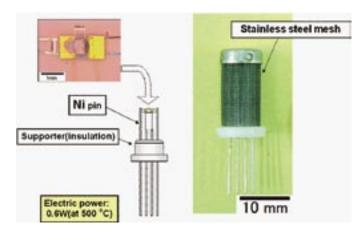
A solid electrolyte is a solid functional material in which single ion species can migrate, and is expected to be a component of rechargeable batteries and chemical sensors for environmental monitoring. Although high-valence cations are generally regarded as chemically stable species with a high charge density compared to mono- and divalent cations, the mobility of high-valence cations in solids is poor due to their strong electrostatic interaction with anions in the solid lattice.

Since 1995, we have succeeded in developing various kinds of high tri- and tetravalent cation conducting solid electrolytes by carefully selecting the migrating cation species, the crystal structure, and the constituent ion species. As a result, we have achieved extraordinarily high ion conductivities, comparable to those of the commercially used divalent oxide anion  $(O^2)$  conducting solids of yttria-stabilized zirconia (YSZ). In particular, in the case of an  $Al^{3+}$  ion conducting solid, we have realized a practical solid electrolyte  $((Al_{0.2}Zr_{0.8})_{20/19}Nb(PO_4)_3)$  that shows sufficiently high ion conductivity, chemical stability, and mechanical strength to be suitable for practical applications.

## Development of Smart Gas Sensors

Since the 1990s, the emission of gaseous oxides such as  $CO_2$ ,  $NO_x$ , and  $SO_2$  has been recognized as an extremely serious environmental problem, particularly carbon dioxide ( $CO_2$ ) because of its important role in the greenhouse effect. A smart gas sensing tool would be useful in helping to suppress such emissions. Among several proposed types of gas sensors, a sensor based on a solid electrolyte is one of the most promising candidates from the viewpoint of exact and quantitative *in situ* gas detection.

Recently, we have developed a smart gas sensor that uses the Al3+ ion conducting solid electrolyte  $(Al_{0.2}Zr_{0.8})_{20/19}Nb(PO_4)_3$  as the key component of the sensor element. We have modified this sensor for different sensing roles by changing the auxiliary electrode. The photograph shows the CO<sub>2</sub> gas sensor that we have developed. Since this sensor shows superior CO<sub>2</sub> sensing performance, with a quick and reproducible and theoretical response without any interference from ambient gases or water droplets, we confidently expect it to be a practical tool that can be used wherever CO2 is emitted.



### Development of Novel Catalysts for Environmental Protection

Highly efficient catalysts that can help to clean up automotive exhaust pollutants at low temperatures are actively sought because of recent environmental regulations in Europe, USA, and Japan. In particular, soot is a significant component of air pollution and is harmful to both human beings and the environment. The ability of CeO<sub>2</sub>-based materials to store and release oxygen makes them an important player in the field of oxidation catalysts, especially in automotive catalytic converters. Since the reduction behavior of these materials at low temperatures can reduce the ignition temperature of particulates produced by diesel vehicles, special attention has been paid to the synthesis and characterization of solid solutions based on CeO<sub>2</sub>, which can show excellent redox properties at low temperatures.

We have shown that the formation of ternary  $CeO_2$ - $ZrO_2$ - $Bi_2O_3$  (CZB) solid solutions is significant in promoting effective reduction behavior at low temperatures. In particular, preparation of a CZB solid solution supported on La-stabilized  $\gamma$ - $Al_2O_3$  (CZB/ $Al_2O_3$ ) has the potential to be a key factor in advanced catalytic converters. The low-temperature redox activity demonstrated by the CZB/ $Al_2O_3$  catalyst, which is effective at temperatures below 100 °C, has never been attained in conventional catalysts without the help of precious metals. Furthermore, the redox activity of the catalyst was promoted by the addition of silver, which is a well-known oxygen-permeable component. Silver's promotion of the redox activity can be attributed to both the increase in oxygen-deficient species in the near-surface layer, which was produced by the partial dissolution of Ag into the CZB lattice, and the increase in oxygen mobility from the metal-oxide interaction between silver oxides and CZB on the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support.

### Development of New Environment-friendly Pigments

The use of non-toxic materials in the chemical industry has become a significant area of interest, with the aim of reducing health hazards and environmental damage. However, several popular pigments are

based mainly on toxic transition metals or heavy metal ions. In particular, the most popular inorganic yellow pigments for plastics and paints for traffic markings are CdS (cadmium yellow) and PbCrO<sub>4</sub> (chrome yellow), respectively. For this reason, there have long been efforts to develop environmentally friendly yellow pigments that can replace the conventional ones containing toxic elements. We demonstrate here the synthesis and characterization of environment-friendly inorganic yellow pigments composed of CeO<sub>2</sub>, Bi<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub> and SiO<sub>2</sub>, which are non-toxic materials with the potential to give brilliant color (See photo).



#### References (main papers in 2007)

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- (8) Extraordinarily High Zr<sup>4+</sup> Ion Conducting Solid, N. Imanaka, S. Tamura, and T. Itano, *J. Am. Chem. Soc.*, **129**, 5338-5339 (2007). For other papers, see: http://www.chem.eng.osaka-u.ac.jp/~imaken/