Basicity, Defect Chemistry, and Electronic Structure of Proton Conducting Oxides

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Abstract

In order to develop novel proton conducting oxides for high temperature electrochemical energy devices, the proton incorporation reaction and proton solubility in acceptor doped complex oxide system have been conducted from the view point of acid-base reaction, defect chemistry, and electronic band structure.

Theoretical Background

The reaction for the incorporation of protons in acceptor-doped oxides has been extensively examined by various experimental methods, and the proton incorporation reaction has been well described by the defect chemical reactions.

$$H_2O + V_O + O_O^\times = 2OH_O \qquad (1)$$
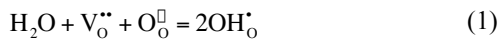
One of the problems in the defect chemical treatment is that the apparent equilibrium constant for the reaction (1) exhibits a strong dopant concentration dependence in some of the oxide systems. Alternative chemical approach is to employ an acid-base rection on the basis of the local configuration of the acid and basic sites.

The authors have been examined the water dissolution reaction from the viewpoint of acid-base reaction. In the previous reports, the hydroxyl capacity, originally proposed by Wagner[1], has been modified for solid oxide system as shown below, and was examined for Yb-doped BaCeO$_3$[2].

$$O^{2-}(g) + 2V_O + H_2O = 2OH_O \qquad (2)$$
$$C'_{OH} \equiv [OH_O]/[V_O] \cdot p_{H_2O}^{1/2} \qquad (3)$$
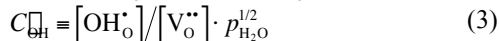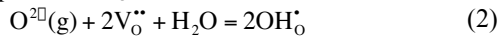
As shown in Fig. 1, the hydroxyl capacity stays at almost constant value against BaO activity, indicating the chemical potential of O^{2-}, which is an index of the basicity of complex oxide, is constant. The variation of BaO potential is governed by the Ba^{2+} potential determined by the variation of vacancy concentration on Ba-site.
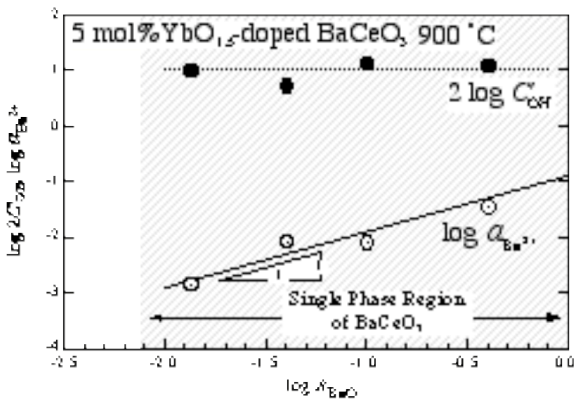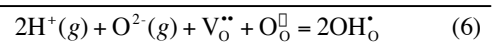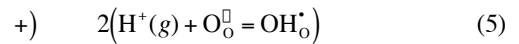

Fig. 1 Variation of hydroxyl capacity, log C'_{OH}, and log $a_{Ba^{2+}}$ as a function of log a_{BaO}.

In the present article, the local basicity proposed in a generalized form by Maier[3] is been newly defined by employing the combination of partial acid-base (neutralization) reactions of the acid and basic site based on the electronic band structure of the corresponding systems determined by electron spectroscopic measurements, such as PES, R-PES, XAS, and SXES.

The water dissolution reaction (Eq. (1)) is divided into the following partial acid base reactions.

$$O^{2-}(g) + V_O = O_O^\times \qquad (4)$$
$$+)\quad 2(H^+(g) + O_O^\times = OH_O) \qquad (5)$$
$$\overline{2H^+(g) + O^{2-}(g) + V_O + O_O^\times = 2OH_O \qquad (6)}$$

Charged ionic gas species are related to water gas molecule by the following equation.

$$H_2O(g) = 2H^+(g) + O^{2-}(g) \qquad (7)$$
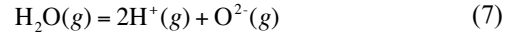
V_O and $O_O^\times$ in Eq's (4) and (5), respectively, corresponds to the most acidic site and the most basic one relative to reacting ions. We employ the definition of the basicity by Lux where the electrochemical potential of gaseous oxide ion (O^{2-}) is used as index of basicity. Through the chemical equilibrium below, the relative electrochemical potential is related to the electron energy (electrochemical potential of electrons: $\eta_{O^{2-}}$);

$$O^{2-}(g) = \tfrac{1}{2}O_2(g) + 2e' \qquad (8)$$
$$\eta_{O^{2-}} = \tfrac{1}{2}\mu_{O_2} + 2\eta_{e'} \qquad (9)$$
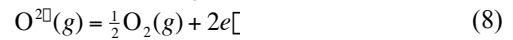
Results and Discussion

The estimated energy diagram for In-doped CaZrO$_3$ is shown in Fig. 2. From the O1s soft X-ray absorption spectroscopy (XAS), the acid site for acceptor-doped oxides is estimated as a defect induced level mainly composed of anti-bonding state of host cation orbital. In the case of CaZrO$_3$, a deformed level of Zr4d (t2g) orbital located below the conduction band is estimated as an acid site (center). Upon introduction of water into the system, as DOS of LUMO level decreases by the occupation of the oxide ion vacancy, V_O, by O^{2-} through the reaction (4), V_O is estimated as the acid center. If all the acid sites are fully neutralized, oxide ion bonding to acceptor cation is considered as a basic center, which is neutralized by protons through the reaction (5). It is estimated that the acid and basic sites are identical on the oxide ion sub-lattice in most of perovskite oxides, but may be different in some other oxides such as fluorite type oxides. Further discussion will be given based on the results of electron spectroscopy and hydroxyl capacity measurements.
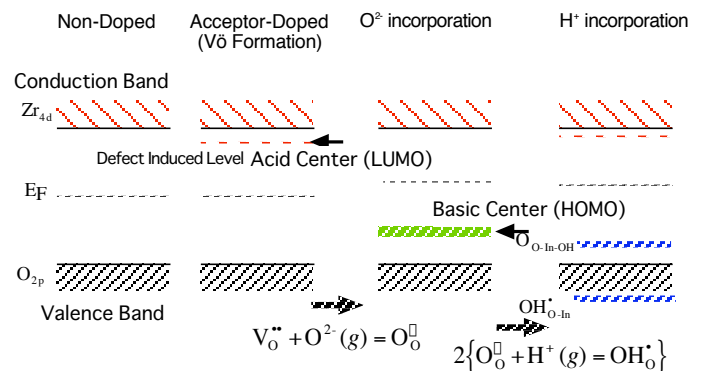

Fig. 2 Schematic illustration of electron energy diagram.

References

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[2] S. Yamaguchi et al., Solid State Ionics, **136-137**, 191 (2000).
[3] J. Maier, Chemistry—A European Journal, **7**, 4762 (2001).