RESEARCH ACTIVITIES

Study on Hydride Ion Conductive Materials for Novel Electrochemical Devices

Hydrogen has a charge flexibility and can take various charge states such as proton (H⁺), atomic hydrogen (H₀), and hydride (H⁻) depending on the different bonding states in materials. Due to this feature, whereas hydrogen diffusing in metals behaves a state close to H₀, H⁺ becomes the charge carrier in many types of chemical compounds, including polymer, solid acid, MOF, and ceramics. In the former case, hydrogen absorbing alloys and hydrogen embrittlement of metals have been studied, and in the latter case, materials research for fuel cell applications has been actively carried out over the past few decades. In contrast, H⁻ is a relatively rare state that can only be taken when hydrogen is coordinated to metals with low electronegativity such as alkali metals and was not well recognized as a charge carrier. Therefore, even though H⁻ has attractive features such as suitability for fast ionic conduction in terms of size, valence, and polarization and strong reduction properties (Eº(H⁻/H₂) = −2.35 V vs. SHE), its electrochemical applications have not been considered. Against this background, we developed a series of H⁻ conductive oxyhydrides, La₂₋ₓSrₓLiH₁₋ₓO₃₋ₓ, in 2016 and found its function as an H⁻ solid electrolyte for the first time. Based on the results, our group is challenging the progress of materials science on H⁻ conductors and the development of novel electrochemical devices utilizing H⁻ conduction phenomena.

Figure 1. Our research concept toward realization of electrochemical devices utilizing hydrogen charge flexibility.

Selected Publications
1. Study on $H^-$ Conductive Oxyhydrides$^{1-3}$

In 2016, we synthesized a series of $K_2NiF_4$-type oxyhydrides, $La_{2-x}Sr_xLiH_{1-x-y}O_{3-y}$ (LSLHO), which are equipped with anion sublattices that exhibit flexibility in the storage of $H^-$, $O^{2-}$, and vacancies (Figure 2 upper) and demonstrated pure $H^-$ conduction properties in the oxyhydrides.$^{13}$ The Li-based oxyhydrides acted as solid electrolytes and the all-solid-state Ti/LSLHO/TiH$_2$ cell showed a redox reaction based on hydrogen storage/desorption on the electrodes, which is a first battery reaction using $H^-$ conduction phenomena.

More recently, we synthesized novel $H^-$ conductive oxyhydrides, Ba$_2$MHO$_3$ ($M = Sc, Y$),$^{2,3}$ with the $K_2NiF_4$-type structure and confirmed its unique site selectivity for $H^-$. In accordance with the electrostatic valence rule, it was found that the hydride ions in Ba$_2$MHO$_3$ selectively occupied the rock-salt layer, in contrast to those of the observed iso-structural Li-based oxyhydrides that preferentially occupy the perovskite layer (Figure 2). The cation size at the octahedral center influences the anion arrangement within the rock salt layer, and in the Y-oxyhydride, the complete ordering of H/O center influences the anion arrangement within the rock salt (Figure 2). The cation size at the octahedral center influences the anion arrangement within the rock salt layer, and in the Y-oxyhydride, the complete ordering of H/O center influences the anion arrangement within the rock salt layer. The cation size at the octahedral center influences the anion arrangement within the rock salt layer, and in the Y-oxyhydride, the complete ordering of H/O center influences the anion arrangement within the rock salt layer.

More recently, we synthesized novel $H^-$ conductive oxyhydrides, Ba$_2$MHO$_3$ ($M = Sc, Y$),$^{2,3}$ with the $K_2NiF_4$-type structure and confirmed its unique site selectivity for $H^-$. In accordance with the electrostatic valence rule, it was found that the hydride ions in Ba$_2$MHO$_3$ selectively occupied the rock-salt layer, in contrast to those of the observed iso-structural Li-based oxyhydrides that preferentially occupy the perovskite layer (Figure 2). The cation size at the octahedral center influences the anion arrangement within the rock salt layer, and in the Y-oxyhydride, the complete ordering of H/O led to the formation of the [Ba$_2$H$_2$] layers. These results indicate that anion ordering in oxyhydrides could be tuned by appropriate element substitutions, which is a new insight for designing $H^-$ conducting materials.

Figure 2. Crystal structures of $H^-$ conductive oxyhydrides $La_{2-x}Sr_xLiH_{1-x-y}O_{3-y}$ ($x = 0, y = 0, 1, 2$) and Ba$_2$MHO$_3$ ($M = Sc, Y$).

2. Materials Processing of Oxyhydrides for Electrochemical Applications$^{4-6}$

Synthesizing oxyhydrides usually requires unique methods such as solid-state reactions at high-pressure and topochemical reactions using CaH$_2$ reductant. Since the former method is a sealed reaction system, loss of light elements, such as hydrogen, can be prevented, making it a suitable synthesis method for composition control and, ultimately, exploration for new materials. On the other hand, the latter is an $O^{2-}/H^-$ exchange reaction using oxides as precursors and is useful for preparing metastable phases that the conventional sintering process cannot obtain. However, the low synthesis volume in the high-pressure method and less reproducibility of composition due to complicated multi-step processes such as washing in CaH$_2$ reduction have prevented expanding the study on oxyhydrides to applicable research for electrochemical devices. To resolve the above problems, we have been trying to establish a suitable synthesis method for oxyhydrides.

For Li-based oxyhydrides (LSLHO) with the $K_2NiF_4$-type structure, we have successfully established the solid-state reaction method under ambient-pressure.$^{5,6}$ Electro motive force measurements using hydrogen concentration cells became possible by preparing the LSLHO sintered pellets with sufficient size.

We have also succeeded in direct synthesis of barium titanium oxyhydride BaTiO$_3$·$H_x$ by mechanochemical reaction, allowing gram-scale and speedy preparation of the functional material. Its unique reaction condition without external heating might be suitable for materials exploration of oxyhydrides. We also confirmed that the prepared polycrystalline BaTiO$_3$·$H_x$ worked as a hydrogen-permeable electrode. This result suggests that $H^-/e^-$ mixed conducting oxyhydrides are promising for electrode use in electrochemical chemical/energy conversion devices (Figure 3).$^{6}$

Figure 3. BaTiO$_3$·$H_x$ synthesized by a mechanochemical method and its performance as hydrogen permeable electrodes.

References
4) A. Watanabe, G. Kobayashi* et al., Electrochemistry 85, 88–92 (2017).

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