論文の内容の要旨

Abstract of Dissertation

Processing and Transport Properties of Nanograined Oxide Protonics Materials with Perovskite Structure

(ナノ構造を有するペロブスカイト型酸化物プロトニクス材料合成プロセスと輸送特性)

せるべら　りんり　ぶっち　まんぐろーばん

Cervera Rinlee Butch Mangrobang

ABSTRACT

Solid oxide fuel cell (SOFC) is a promising future technology for a highly efficient, fuel flexible, and clean source of energy. SOFC using oxide protonics materials, has obtained more interests as compared to traditional SOFC with oxide ion conductors due to its possible low temperature of operation between 400^{o}C to 700^{o}C which is a desirable temperature range for both chemical and energy conversion processes in view of combined system with steam reforming reactions. The search for a good solid electrolyte with high protonic conductivity accompanied with high mechanical and chemical stability is the foremost challenge for the realization of this intermediate temperature solid oxide fuels cells. One approach is either to continue searching for new materials or the other is to engineer the existing ones in order to enhance their specific properties. Considering the latter choice, one exciting and promising way which is still a virtually untapped area is the nano-scaled structuring of proton conducting solid electrolytes. Combining the superior characteristics of nanosized grain materials with the proton conducting properties of solid oxides is an interesting strategy that may show different properties in contrast to its large grain counterparts.

This PhD work mainly focuses on developing nanostructured proton conducting solid electrolytes for intermediate temperature solid oxide fuel cells. The key motivation is to answer whether nanocrystalline materials with its renowned superior characteristics will help in enhancing the properties of the existing oxide solid electrolytes and in the process gaining an understanding of the so-called 'nanoionics' phenomena. The objective seems easy. However, obtaining a nanosized grain samples with the

desired stoichiometry and structure is a challenge especially with multinary metal oxide system and with the existing synthetic techniques typically employed (i.e. classical solid state reaction). Hence, this PhD research started from developing new synthetic processes in order to obtain nanosized grain complex metal oxides at very low processing temperatures.

Solid electrolytes for intermediate temperature solid oxide fuel cells (IT-SOFC) applications are usually complex multicomponent metal oxides. The typically studied are those of acceptor-doped ABO_3 type perovskite structures. In principle, protonic defects can be incorporated in the ABO_3 lattice structure in the form of hydroxyl anions as replacement for oxygen vacancies created by the acceptor dopant on the B-site sublattice, whereas a new and interesting strategy for incorporation of protonic defects is to incorporate these defects in-situ during crystallization by employing low temperature synthetic processes. Here, instead of creating oxygen vacancies for charge compensation, the normal lattice oxygen is replaced by protonic defects. This is one of the basic ideas of this PhD that drives us in finding materials that is stable under the co-existence of protonic defects at intermediate temperatures.

The first part of my Ph.D. research is the successful development of a new synthetic process to synthesize nanograined materials within just several nanometers at temperatures about 350^{o}C with an in-situ incorporation of protonic defects. This process is especially advantageous in synthesizing complex metal oxides with the goal of obtaining nanosized grain powders fully incorporated with protonic defects. Using high pressure pressing (4GPa) fully compacted (no porosities) bulk-nanograined samples of rare-earth doped $BaZrO_3$ have been achieved even at room temperature.

Having a synthetic process as a key tool to obtain nanograined solid electrolytes, synthesis of different types of protonic conductors and even creation of new class of oxide protonics materials are examined. Important new findings not only about protonic conduction of nanograined rare-earth doped $BaZrO_3$ and other material properties for nanocrystalline solid electrolytes have been obtained but interestingly, new types of protonic conductors stable only at intermediate temperatures but decompose at higher typical processing temperatures (>1000^{o}C) has also been found. $BaScO_2(OH)$, an ABO_3 perovskite type metal oxide where one third of the oxygen in the lattice is replaced by OH forming a new general $ABO_2(OH)$ type compound termed as hydroxyperovskite, has been successfully synthesized at low processing temperature (<400^{o}C) using a newly developed synthetic approach. With the combined results, basic ideas have been formulated for nanograined oxide protonic conductors.

In this dissertation, in the case of complex metal oxide like rare-earth doped $BaZrO_3$ synthesize via wet chemical process, the effect of nanosized grain (several nm) solid electrolyte is first dictated by the thermodynamic stability of the phases at low processing temperatures with water. In the case of Y-doped $BaZrO_3$, real doping with the desired stoichiometry for nanosized grain is difficult to achieve. Even with Sc-doped $BaZrO_3$, the different competing formation of the $BaZrO_3$ and $BaScO_2(OH)$ creates a mixed phases of this solid electrolyte. Upon high pressure pressing, the high amount of surface adsorbed water species of the nanocrystals will increase its water activity due to the induced high pressure and will attack the surface cations forming a thin amorphous grain boundary core. Whether such amorphous phase at the grain boundary core is decomposed upon heat treatment at intermediate temperatures (300-600^oC) depends on thermodynamics of phase formation and kinetics, hence, if not will create a blocking path for protonic motion. In the case of $BaScO_2(OH)$, the relatively easy reaction of the pressed induced hydroxides of Ba and Sc at the grain boundary core as detected by FTIR and TG/DTA can easily transform again to the original phase at intermediate temperature (<350^oC) which explain the high protonic conductivity (10^{-3} S/cm) of this new class of nanosized grain oxide protonics materials.

For Y and Sc-doped $BaZrO_3$ case, upon annealing at higher temperatures, extraneous phases are desorbed and amorphous grain boundary phases are swept by grain growth and those different phases will merge forming the desired stoichiometric compound. Hence, a dramatic increase of the conductivity is noticed for both Y and Sc-doped $BaZrO_3$ upon annealing whereby real desired doping is achieved. From the results, even with 50 nm grain size samples, a high total protonic conductivity has been observed.

In this PhD research work, an important step towards exploring the nanoscience behind nanograined oxide proton conducting solid electrolytes –which can also be generally applied to most nanograined advance ceramics– has been studied and discussed. The findings of this PhD research will surely open new pathways for synthesizing new nanosized grain functional materials thermodynamically stable to be formed at low processing temperatures with the used of the developed approach. Other classes of hydrated phases and oxides stable under the coexistence of protonic defects are still probably out there waiting to be explored. Understanding the nanosized oxide protonics materials may open a new frontier and opportunities in combining nanotechnology with energy related devices for future technology applications.