Preparation of Proton Conductive $CaZr_{1-x}In_xO_{3-a}$ Thin Films by CVD-EVD Method

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Recent worldwide interests in energy and environmental problems have accelerated R&D of fuel cells because they are clean and silent and they also have high efficiency of energy conversion. In several fuel cell systems, polymer electrolyte membrane fuel cells (PEMFCs) that can operate at room temperatures, in particular, have received much attention.

It is well known that pure hydrogen gas is desirable as a fuel for long-time operation of PEMFCs. Hence, on-site ultra high pure hydrogen production systems are prerequisite for a widespread use of PEMFCs systems. Hydrogen production systems containing proton conductive solid electrolytes will be one of the most appropriate methods for the on-site hydrogen production systems mentioned above. This is because proton conductive solid electrolytes can transport hydrogen selectively by electrochemical methods and then they can separate hydrogen gas from reforming gases (including H_2, CO, CO_2, CH_4, etc.) of LNG, gasoline, etc. Moreover, proton conductive solid electrolytes are not so expensive compared to hydrogen permeation membranes such as Pd-based membrane.

Many kinds of proton conductive solid electrolytes have been already reported [1, 2]. Among them, $CaZr_{0.9}In_{0.1}O_{3-a}$ possesses higher tolerance toward CO_2, and therefore it is a promising candidate for the above-mentioned system [3]. One of the drawbacks of $CaZr_{0.9}In_{0.1}O_{3-a}$ is its low proton conductivity. Hence, the thin film of this material is required to decrease the proton conduction resistance, resulting in increase of the hydrogen evolution efficiency.

In this work, we prepared $CaZr_{1-x}In_xO_{3-a}$ thin films on porous NiO substrates by chemical vapor deposition (CVD)-electrochemical vapor deposition (EVD) method for the first time. This CVD-EVD method can give quite dense and uniform thin films on porous substrates.

The CVD-EVD system applied in this work has been reported precisely elsewhere [4]. We used $CaCl_2$, $InCl_3$ and $ZrCl_4$ as source materials. The thin films were deposited on porous NiO substrates at 1273 K for 2 h. The NiO substrate can release oxygen at high temperatures and then serves as an oxygen source. Prepared thin films were characterized by X-ray diffraction measurement, scanning electron microscopy, X-ray photoelectron spectroscopy, and electron prove micro analyzer.

Figure 1(a) shows an XRD pattern of the thin film deposited on a porous NiO substrate. Although some peaks due to impurities were observed in this pattern, many diffraction peaks were in good agreement with a $CaZr_{0.9}In_{0.1}O_{3-a}$ pellet (TYK Co., Fig. 1(b)), indicating that $CaZr_xIn_{1-x}O_{3-a}$ thin films were prepared by CVD-EVD method.

Figure 2 shows a top-view SEM image of the thin film deposited on a NiO substrate. Prepared thin film showed quite dense surface structure and showed no pinholes on the film surface. These are typical features of thin films prepared by CVD-EVD process.

From these results, we found that proton conductive $CaZr_{1-x}In_xO_{3-a}$ thin films can be prepared by CVD-EVD method. Proton conductivity of the resultant thin film will be discussed in the presentation.

References

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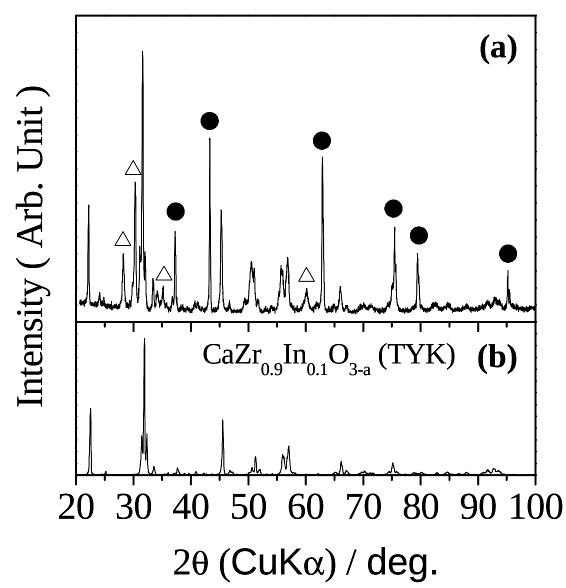

Fig. 1. XRD patterns of (a) a Ca-Zr-In-O thin film deposited on a porous NiO substrate at 1273 K for 2 h. (close circles : NiO, open triangles : impurities) and (b) a $CaZr_{0.9}In_{0.1}O_{3-a}$ pellet produced by TYK.

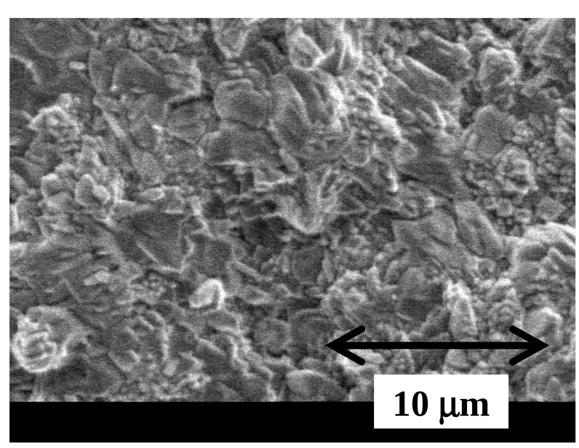

Fig. 2. Top-view SEM image of a thin film deposited on a porous NiO substrate at 1273 K for 2 h.