DEVELOPMENT OF PROTON-CONDUCTING OXIDES FOR HYDROGEN
SEPARATION MEMBRANES

Gaye ÖZDEMİR1,2, Taner ÖZDAL1,2 and Fatih PIŞKİN1,2
gayeozdemir@posta.mu.edu.tr

1Dept. of Metallurgical and Materials Engineering, Muğla Sıtkı Koçman University, Muğla, TURKEY
2Energy Materials Laboratory, Muğla Sıtkı Koçman University, Muğla, TURKEY

There is growing interest in renewable energy sources and their applications. In this regard, there are remarkable developments in hydrogen technology i.e. hydrogen storage and transportation. Injection of hydrogen into the natural gas pipeline is one of the approaches accepted for easier storage and transportation. Figure 1. Infrastructural studies related to hydrogen injection into the natural gas pipeline are also carried out in Turkey [1]. Undoubtedly, hydrogen purification will be required in order to recover hydrogen from the gas mixture, i.e. natural gas and hydrogen when it is required. This project accordingly is aimed to develop composite separation membranes based on proton-conducting oxides for hydrogen recovery.

Figure 1. Projection of Power-to-Gas [2].

Considering the production sources of hydrogen, it dominantly depends on fossil fuels, Figure 2.

Figure 2. Distribution of resources used for hydrogen production [3].

Hydrogen production methods, which are frequently used today, a purification is always needed after hydrogen production, Figure 3.

Figure 3. Hydrogen production methods [4].

There are mainly three methods for hydrogen purification for hydrogen. These are: pressure swing adsorption, cryogenic distillation and hydrogen separation membranes. Among them membrane-based process offers small- and large-scale application and relatively low-cost hydrogen separation.

Hydrogen separation membranes are typically based on Pd and its alloys [10]. However, hydrogen embrittlement problem in Pd and the high cost of Pd alloys restricts their usage for industrial applications.

Metal-oxides, especially perovskite structure, are of great interest because of their superior hydrogen selectivity (theoretically infinite). In addition, perovskite structured oxides are inexpensive compared to Pd-based membranes [11].

Figure 4. Ideal perovskite (ABO3) structure [6].


Table 1. Goldschmidt tolerance factor [13] calculations for the compositions proposed in the project.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Goldschmidt Tolerance Factor</th>
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<tbody>
<tr>
<td>BaCe0.95Y0.05O3.5</td>
<td>0.856</td>
</tr>
<tr>
<td>SrZr0.95Y0.05O3.5</td>
<td>0.9432</td>
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Equation 1. Goldschmidt tolerance factor.

Hetero-structures typically increase the oxygen vacancy concentration in perovskite oxides, which has a critical role in proton conduction [12], Figure 7. In this study BaCe0.95Y0.05O3.5 and SrZr0.95Y0.05O3.5 are chosen as a model composite system in order to investigate the effect of hetero-structure on the proton conductivity in these types of oxides.

Figure 5. Hydrogen purification in proton-electron-conducting perovskite oxides [7].

Composite with BCY:SZY ratios of 0.75:0.25, 0.50:0.50 and 0.25:0.75 are investigated in this study to reveal the effect of hetero-interfaces on the proton conductivity. Each oxides is produced using the Pechini method with the following parameters, Figure 8.

Figure 6. Hydrogen transition mechanism seen in perovskite structured oxides in humid environments [8].

Figure 7. Formation of heterointerface in proton-conducting oxides [9].

Figure 8. Synthesis parameters applied in the study.

Figure 9. XRD patterns of synthesized BCY (TM:CA:1:1.5) and SZY (TM:CA:EDTA, 1:2:1) powders calcined at 1100 °C, 1200 °C and 1300 °C for 5 hours.

References
[1] Erenjele Aroma Bulutumayan, Ock 2020
[2] European Power to Gas Platform, 2018
[8] Hashim vd., 2018

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