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A thermodynamically stable $La_2NiO_{4+\delta}$/ $Gd_{0.1}Ce_{0.9}O_{1.95}$ bilayer oxygen transport membrane in membrane-assisted water splitting for hydrogen production

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Abstract

A bilayer configuration of mixed ion-electron conducting $La_2NiO_{4+\delta}$ and oxygen-ion conducting $Gd_{0.1}Ce_{0.9}O_{1.95}$ (LNO/GDC10) was proposed for hydrogen production by water-splitting and its properties were measured as a function of temperature, reducing gas CO content and water vapor pressure during the hydrogen production by water-splitting. The hydrogen production flux increased with increasing water vapor pressure and oxygen chemical potential to a maximum of 0.12 cm^3 (STP)/min-cm^2 with 23.25% CO/76.75% CO_2 (40 sccm)/balance He (60 sccm) gas mixture on the oxygen-permeate side and wet N_2 ($pH_2O=0.49$ atm) on the oxidizing side at 900 °C. The stability of the bilayer membrane was tested in a very low oxygen partial pressure (pO_2) on the oxygen-permeate side. The presence of GDC10 on the oxygen-permeate side of the bilayer prevented the direct exposure of LNO to very low pO_2 and thus protected it from decomposition, even at $pO_2 \approx 10^{-15}$ atm.

Keywords: $La_2NiO_{4+\delta}$/ $Gd_{0.1}Ce_{0.9}O_{1.95}$ bilayer; Water-splitting; Hydrogen production; Membrane-assisted water splitting for hydrogen production

1. Introduction

Inorganic membranes have been extensively studied for hydrogen production and purification due to the ever increasing demand for high purity hydrogen in fuel cells, and petrochemical and semiconductor applications [1–5]. Among these inorganic membranes, mixed ion-electron conducting (MIEC) dense ceramic membranes have attracted major attention for gas separation applications [1,3,5–7] because of their ability to separate oxygen from a gaseous mixture by non-galvanic ambipolar transport of oxygen from the high oxygen partial pressure side (pO_2) to the low pO_2 side, when placed in a chemical potential gradient of oxygen. Moreover, when MIEC membranes are coupled with the water dissociation process, they can be utilized for hydrogen production at even moderate temperatures by selectively removing oxygen from the reaction system in Eq. (1)

$$H_2O \leftrightarrow H_2 + \frac{1}{2}O_2 \quad (1)$$

by non-galvanic ambipolar transport of oxygen and, thereby, shifting the thermodynamic equilibrium of the reaction to the product side [1,6,7]. Since the membrane-assisted water-splitting for hydrogen production (MWHP) is a direct result of oxygen permeation through membranes, the oxygen permeation rate is an important factor in determining the hydrogen production rate.

The factors affecting the oxygen permeation rate and, in turn, the hydrogen production rate by water-splitting include (i) ambipolar (oxygen ion and electron) conductivity, (ii) pO_2 gradient across the membrane, (iii) temperature, (iv) membrane thickness, and (v) surface oxygen exchange kinetics [7,8]. For MWHP using MIEC membranes at moderate temperatures, the creation of a high pO_2 gradient across the membrane is an important factor. However, as the equilibrium constant of reaction in Eq. (1)

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is very small [9], the actual concentration of oxygen formed by water-splitting and the resultant pO_2 on the oxidizing side are very small in magnitude. Therefore, to create a high pO_2 gradient across the membrane, the pO_2 on the reducing side of the membrane should be lower in the magnitude than the pO_2 of the oxidizing side. In the past, most MWHP research has focused on proving the working principle of hydrogen production using MIEC membranes without paying greater attention to the thermodynamic stability of these membranes during the operation [1,6,10]. However, the requirement for very low pO_2 on the reducing side of the oxygen permeation membrane creates a major challenge for the application of MIECs in MWHP, as MIECs are prone to decomposition at very low pO_2, which raises serious concerns about the thermodynamic stability of such membranes in working environments [11,12]. In this study, we have addressed the problem of the thermodynamic stability of MIEC membranes during MWHP by utilizing the concept of bilayered membrane using lanthanum nickel oxide ($La_2NiO_{4+\delta}$, LNO) as an MIEC material.

LNO with K_2NiF_4-type structure exhibits one of the highest oxygen permeation fluxes among alkaline-earth metal cation-free membrane materials [13]. Apart from their high oxygen permeability, LNO-based materials offer additional advantages of moderate thermal expansion that is compatible with glass-ceramic sealants and stainless steel, very low chemically induced stress and reduced interaction with gaseous species such as CO_2 due to the absence of alkaline-earth cations. Therefore, as we have previously reported [14], the LNO-based MIEC materials have potential for application in oxygen separation membranes. However, like other MIEC materials, LNO suffers from instability in low pO_2 environment [15,16]. Therefore, in order to overcome the limited thermodynamic stability of LNO in a low pO_2 atmosphere during MWHP, in the present work, we demonstrate the concept of a bilayer membrane consisting of LNO and 10% gadolinium-doped ceria ($Gd_{0.1}Ce_{0.9}O_{1.95}$, GDC10). In a bilayer structure, as shown in Fig. 1(a), the gradient within each layer is determined by the relative thickness and transport property of the individual layer [11], so that the local oxygen activity at the material interface between LNO and GDC10 can be increased by increasing the thickness of the GDC10 layer relative to the LNO layer. In this way, the pO_2 at the GDC10/LNO interface can be increased to a point where the LNO alone would be thermodynamically unstable in a reducing atmosphere. Therefore, by using a 'protective layer' of GDC10 on the reducing gas side, the stability of the otherwise thermodynamically unstable LNO-based material in a reducing atmosphere is ensured, as it is not exposed directly to a lower pO_2 and the consequent LNO decomposition. LNO is used as the MIEC in the present study due to its high oxygen permeation rate as compared to the other MIECs that are relatively more stable in low pO_2, such as $La_{0.7}Sr_{0.3}Cu_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF7328) [1]. Although LNO decomposes at higher pO_2 than LSCF7328, its oxygen

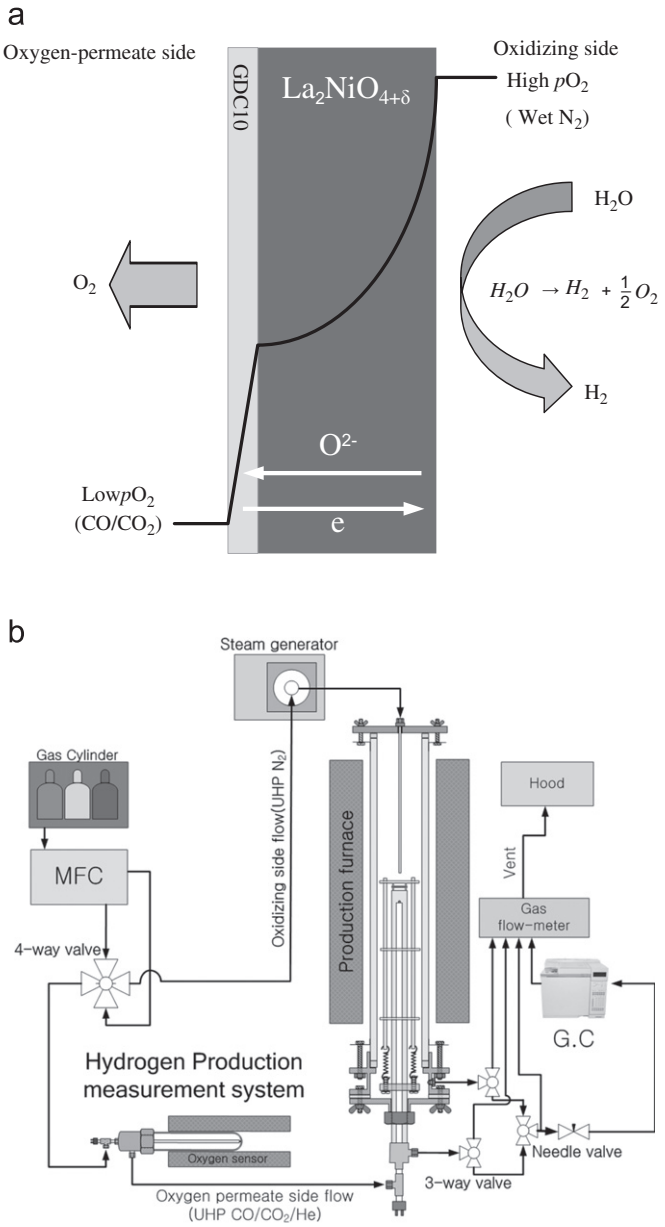

Fig. 1. Schematic diagram of (a) the operation of LNO/GDC10 bilayer membrane in hydrogen production using water splitting and (b) the experimental set-up of hydrogen production from water splitting using LNO/GDC10 bilayer membrane.

permeation rate is higher than that of LSCF7328, when compared under a thickness-normalized condition (≈ 0.954 mm) at different temperatures [14]. Ceria-based solid oxides show a higher stability in a very low pO_2 atmosphere [17] and are normally used as oxide ion-conducting electrolytes. However, they easily develop n-type electronic conduction at high temperatures and low pO_2 [18]. Therefore, the use of GDC10 in bilayer fabrication not only improves the compatibility between the LNO and GDC10 layers under reducing conditions but also ensures good ambipolar diffusion of oxygen in the bilayer membrane. In this work, a LNO/GDC10 bilayer is fabricated by slurry coating method and then investigated