



Ru-doped barium strontium titanates of the cathode for the electrochemical synthesis of ammonia

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ABSTRACT

Ru-doped barium strontium titanate (BSTR) perovskites ($\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Ti}_{1-x}\text{Ru}_x\text{O}_{3-\delta}$, $x = 0, 0.05, 0.1$) (BSTR) were evaluated as cathode materials for the electrochemical synthesis of ammonia from wet H_2 and dry N_2 . Phase crystallinity and the electrochemical properties of BSTR were analyzed. The BSTR structure is stable in low oxygen partial pressure, possibly as a result of its cubic nature. Doping Ru on the B-site of the BST improves its electrochemical properties, because increasing replacement of Ti^{4+} by Ru^{4+} causes a decrease in ohmic resistance. Introduction of Ru^{4+} ions on the B-site of the BST increased catalytic activity for the ammonia synthesis reaction. An electrochemical cell using BSTR as the cathode ($\text{Ni}/\text{BaCe}_{0.4}\text{Zr}_{0.4}\text{Y}_{0.2}\text{O}_3$ (BCZY)/BCZY/BSTR) exhibits a maximum ammonia formation rate of $1.1 \times 10^{-9} \text{ mol s}^{-1} \text{ cm}^{-2}$ and a Faradaic efficiency of 5.9% at 500 °C under an applied voltage of 1.2 V; short-term stability tests showed high stability.

1. Introduction

Ammonia (NH_3) is commonly used in the synthesis of a variety of products such as fertilizers [1], explosives [2] and pharmaceuticals [3]. In addition, ammonia is expected to have an important role in future energy storage technologies because of its high energy density [4].

Ammonia is commercially synthesized using the Haber-Bosch process; however, there are a number of critical disadvantages of using this synthesis method. The ammonia conversion reaction is favored under high temperature and pressure ($150 \leq P \leq 300 \text{ bar}$) [1,5–7]. Therefore, an alternative route has been suggested to synthesize ammonia using a proton-conducting electrolyte (H^+) cell at atmospheric pressure, in which the above disadvantages of high pressure are eliminated [7]. Electricity supplied to the cell separates the protons from the steam at the anode, at approximately $400 \leq T \leq 700 \text{ °C}$, and drives them through the proton-conducting electrolyte layer to react with N_2 adsorbed on the surface of the cathode thus producing ammonia [8–10]. The cell components for the electrochemical synthesis of ammonia consist of an electrolyte, an anode and a cathode. Ba-containing oxides such as $\text{BaCeYO}_{3-\delta}$ and $\text{BaZrYO}_{3-\delta}$ are used as the proton-conducting electrolyte materials. $\text{BaCe}_{0.4}\text{Zr}_{0.4}\text{Y}_{0.2}\text{O}_{3-\delta}$ (BCZY) for example, has been developed as an electrolyte, and exhibits reasonable proton conductivity and excellent stability [11]. Ni cermet mixed with the electrolyte material can be used as the anode [12]. Pd–Ag alloy is

frequently used as the cathode material, because Pd exhibits high selectivity to ammonia [13–16] due to its ability to dissociate the N–N bond, which is the rate determining step (RDS) in ammonia synthesis [17,18], when combined with hydrogen. However, the use of precious metals is expensive and they tend to lose surface area under operating conditions. Thus, new cathode materials with adequate catalytic activity to replace Ag–Pd cathodes are being sought.

Recently, perovskite-based materials have been found to be attractive candidates with excellent stability, suitable electrochemical catalytic activity, and low cost compared to precious metals. Perovskites have various physical properties depending on the doped elements. Among the perovskites, many ferrite-containing perovskite materials have been studied due to their inherent activity for ammonia synthesis reactions [19–23]. Cobalt based ferrite-containing perovskites materials, such as $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (LSCF) and $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (BSCF), have been developed as cathodes, and exhibit high electrochemical performance for the electrochemical ammonia synthesis [12,24]. However, these perovskite materials are not suitable because they are unstable under the cathodic conditions (low oxygen partial pressure) because cobalt is highly volatile and easily reduced [25–28]. Therefore, enhancing the stability of the cathode during the electrochemical synthesis of ammonia needs to be studied.

$\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_{3-\delta}$ (BST) has received attention due to its remarkable structural stability, and good proton conductivity [29–32]. Moreover,

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