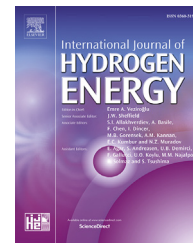




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Ammonia synthesis at intermediate temperatures in solid-state electrochemical cells using cesium hydrogen phosphate based electrolytes and noble metal catalysts

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ABSTRACT

This work reports the electrochemical synthesis of ammonia in solid-state cells at 220 °C and atmospheric pressure. Composites of CsH₂PO₄ and SiP₂O₇ were used as the electrolyte, and Pt/C-loaded carbon paper was employed as the anode. Five kinds of electrode materials, including Pt/C-, Pt-Ru/C-, Ru/C-, Ru- and Ag-Pd-loaded carbon paper, were examined as the cathode. Electrochemical activities of the cathode materials were evaluated by cyclic voltammetry. Both H₂ and steam were used as the hydrogen source. The successful synthesis of ammonia was confirmed using Nessler's solution. When H₂ was used as the hydrogen source, ammonia formation rates higher than 10⁻¹⁰ mol cm⁻² s⁻¹ were obtained using Pt/C- or Ru-loaded carbon paper as the cathode. When steam was used as the hydrogen source, ammonia formation rates higher than 10⁻¹¹ mol cm⁻² s⁻¹ were obtained using Pt-Ru/C- or Ru/C- or Ru-loaded carbon paper as the cathode. Ru and Ag-Pd were the most promising noble metal catalysts for electrochemical synthesis of ammonia from N₂ and steam.

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Introduction

Electrochemical synthesis of ammonia has been receiving considerable attention nowadays due to its potential to convert renewable electrical energy to chemical energy in

ammonia [1–4]. Electrochemical synthesis of ammonia can be achieved at much lower temperatures or pressure compared to conventional Haber-Bosch process [5–7], in which ammonia is produced from the reaction between N₂ and H₂ on Fe-based catalysts at high temperature (about 500 °C) and high

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pressure (15–30 MPa) with a low equilibrium conversion of about 15% [8]. Ammonia is used in the production of synthetic fertilizers, which play a critical role in the world's food supply [9,10]. Furthermore, ammonia is also a possible hydrogen carrier with various advantages, such as ease in storage and transport and high volumetric energy density [11–13]. Ammonia and ammonia-based materials such as hydrazine, ammonia borane, metal ammine salts are carbon-free energy sources at the end users [13]. For example, ammonia borane, which is solid at ambient conditions, has high potential for chemical hydrogen storage [14–16]. Hydrogen stored in ammonia borane can be released through catalyst-assisted hydrolysis reaction at room temperature [17–20]. However, the development in the field of electrocatalytic ammonia synthesis has been hindered by a lack of good electrocatalysts for nitrogen reduction [21]. Theoretical calculations showed that mononitrides of V, Zr, Nb and Cr [22,23], and transition metals such as Sc, Y, Ti, Zr, Mo and Fe [24,25] might display promising activity and selectivity towards nitrogen reduction vs. hydrogen evolution. However, experimental studies using various kinds of electrocatalysts reported ammonia formation rates at least two orders of magnitude lower than the target value of 10^{-6} mol cm^{-2} s^{-1} , which was considered to be economically viable [26], and the corresponding current efficiency was low [27]. Electrocatalysts that selectively reduce N_2 to NH_3 remain elusive [28].

Substantial efforts have been invested in synthesizing ammonia using solid-state electrolytic cells [29–31]. Reactant gases with high N_2 partial pressure (e.g., pure N_2 and air) can be utilized in solid-state electrolytic cells [32] compared to the electrochemical reduction of N_2 in liquid media, such as water [33] and alcohols [34], which have low N_2 solubility. Most recently, Kyriakou et al. provided a comprehensive review of the recent progress in the electrochemical synthesis of ammonia, focusing on both electrode and electrolyte materials [29]. The state-of-the-art solid-state electrolytic cells for ammonia synthesis are operable either below 100 °C (polymer electrolytes) or above 375 °C (carbonate/oxide composites or ceramics) [29,30]. Typical catalysts for N_2 reduction at temperatures lower than 100 °C were Ru [35], Pt [36] and transition metal oxides [37], and those for N_2 reduction at temperatures higher than 375 °C were Ag-Pd [38], perovskite composites [39–41] and transition metal nitrides [42]. However, the electrochemical synthesis of ammonia in solid-state cells at intermediate temperatures of 200–300 °C has not been developed because of the lack of electrolytes with high conductivity and stability. The polymer electrolytes are not applicable at intermediate temperatures due to dehydration or degradation [43], and the ternary carbonate-based composites and ceramics have low conductivity at temperatures below 375 °C [44]. Operation of electrolytic cells at 200–300 °C can provide significant advantages such as lower manufacturing costs, longer life time and more flexible choice of materials [30].

Cesium hydrogen phosphates are a class of solid acids with high conductivity at 200–300 °C, and these compounds have been widely investigated as candidate electrolytes for solid acid fuel cells [45,46]. The composite of CsH_2PO_4 and SiP_2O_7 in a molar ratio of 1: 0.5 exhibited a high conductivity of 66 mS cm^{-1} at 272 °C [47]. This phenomenon was attributed to

the chemical reaction between CsH_2PO_4 and SiP_2O_7 , resulting in the formation of $\text{CsH}_5(\text{PO}_4)_2$ [47]. $\text{CsH}_5(\text{PO}_4)_2$ changed into a molten state above 150 °C, and rendered the composite highly conductive at intermediate temperatures [48]. Furthermore, the $\text{CsH}_2\text{PO}_4/\text{SiP}_2\text{O}_7$ composite was in the solid state at elevated temperatures despite the melting of $\text{CsH}_5(\text{PO}_4)_2$ [49]. In this work, solid-state electrochemical synthesis of ammonia was performed at 220 °C and atmospheric pressure, using the $\text{CsH}_2\text{PO}_4/\text{SiP}_2\text{O}_7$ composite as the electrolyte. Five different electrode materials were prepared and examined in a homemade electrolytic cell. Both H_2 and steam were tested as the hydrogen source. The effects of the applied voltage and cathode material on the ammonia formation rate and current efficiency were investigated.

Experimental

Preparation of $\text{CsH}_2\text{PO}_4/\text{SiP}_2\text{O}_7$ composites

Cesium dihydrogen phosphate, CsH_2PO_4 , was prepared by dissolving stoichiometric quantities of Cs_2CO_3 (99.995% trace metals basis, Sigma-Aldrich) and H_3PO_4 (85 wt% in water, Sigma-Aldrich) in distilled water and drying overnight at 120 °C. SiP_2O_7 was prepared from SiO_2 (AY-200, Tosoh Silica Corporation) and H_3PO_4 as follows [50]. SiO_2 and H_3PO_4 were mixed in a molar ratio of 1: 2.5 and heated at 200 °C for 3 h. The resulting sample was dried at 100 °C for 24 h, then ground into powder and heated at 122 °C for 24 h, and was finally calcined at 700 °C for 3 h to eliminate H_3PO_4 . The as-prepared CsH_2PO_4 and SiP_2O_7 were mixed in a molar ratio of 1: 0.5 and ground for 15 min to form the $\text{CsH}_2\text{PO}_4/\text{SiP}_2\text{O}_7$ composite.

Preparation of electrode materials

Pt/C-loaded carbon paper (Pt loading 1 mg cm^{-2} , Miclab, Japan) was used as the anode in all the experiments in this work. Five kinds of materials were used as the cathode as discussed below: Pt/C-loaded carbon paper (Pt loading 1 mg cm^{-2} , Miclab, Japan), Pt-Ru/C-loaded carbon paper (metal loading 1 mg cm^{-2} , Pt: Ru = 1: 2 in molar ratio, Miclab, Japan), Ru/C-loaded carbon paper, Ru-loaded carbon paper, and Ag-Pd-loaded carbon paper. Preparation of the last three samples is discussed below.

The Ru-loaded carbon paper was prepared by the borohydride reduction method [51], as illustrated in Fig. 1(a). First, certain amounts of $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ (99.98% metals basis, Aldrich) and NaBH_4 ($\geq 90.0\%$, Wako Pure Chemical Industries, Ltd.) were separately dissolved in 50 cm^3 and 25 cm^3 of distilled water. The molar ratio of RuCl_3 and NaBH_4 was 1: 10. Second, the NaBH_4 solution was slowly added into the RuCl_3 solution with stirring, and then the Ru particles, which were generated from the reduction of RuCl_3 by NaBH_4 , were dispersed by ultrasonication for 3 h. Finally, the resultant solution was poured into a filtration device and the Ru particles were deposited on porous carbon paper (TGP-H-120, Toray Industries, Inc.). A hydrophilic PTFE membrane filter with a $0.2 \mu\text{m}$ pore size (JGWP09025, Merck Millipore Corporation) was placed underneath the carbon paper. When the PTFE membrane filter was not used, the filtration took less than

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