



A viable membrane reactor option for sustainable hydrogen production from ammonia



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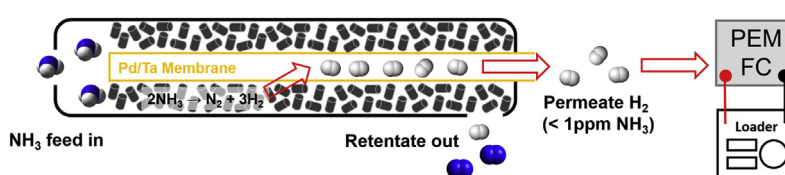
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HIGHLIGHTS

- A compact energy conversion process from NH₃ to electricity is demonstrated.
- Ultra-pure H₂ is produced from NH₃ using novel membrane reactor materials.
- In-situ H₂ extraction allows high conversion of NH₃ at low operating temperature.
- Practical limitations of composite membranes are avoided by pertinent reactions.
- A fuel cell can be operated with as-produced H₂ without any additional purification.

GRAPHICAL ABSTRACT



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ABSTRACT

Conventional hydrogen production from ammonia is both energy and process intensive, requiring high temperature and independent purification units. Here, we present a compact process of energy conversion from NH₃ to electricity using a novel membrane reactor, comprised of a dense metallic Pd/Ta composite membrane and Ru/La-Al₂O₃ pellet catalysts, and a fuel cell unit. The fabricated Pd/Ta composite membrane, having ca. 5 times higher H₂ permeability than conventional Pd-Ag membranes, can both lower NH₃ dehydrogenation temperature and completely remove an additional hydrogen purification unit. Compared to a packed-bed reactor without membrane, ammonia conversion improves by 75 and 45%, respectively at 425 and 400 °C, and > 99.5% of conversion is achieved at 450 °C under pressurized ammonia feed of 6.5 bar. Main barriers of practical application of Pd/Group V metals as a composite hydrogen permeable membrane, embrittlement and durability issues, are overcome owing to pertinent operating temperatures (400–450 °C) of ammonia dehydrogenation coupled with membrane separation. Finally, as-separated hydrogen with < 1 ppm of NH₃ is provided directly to a polymer electrolyte membrane fuel cell, showing no performance degradation for an extended time of operation. The combined results suggest a feasible and less energy/process intensive option for producing hydrogen or electricity from ammonia.

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1. Introduction

Climate change and ever-increasing global energy demand have triggered search for renewable energy solutions [1,2]. Among considered clean and sustainable energy pathways, hydrogen is a promising energy carrier when utilized with fuel cells due to clean by-product (H_2O) and high efficiency [3,4]. However, hydrogen is not naturally abundant and has a low volumetric energy density (2.97 Wh L^{-1} at 0°C , 1 atm), hindering its application to on-site power generation in conjunction with fuel cells. To solve these problems, various liquid chemicals such as formic acid [5,6], ammonia borane [7,8], organic compounds [9–11], etc [12] are being investigated as high capacity hydrogen carriers which can store hydrogen produced from renewable energy sources [13]. Especially, ammonia has exceptionally high hydrogen storage capacity (17.6 wt%, 120 g L^{-1}) [12] and is easy to be stored and transported as a liquid under ambient temperature with moderate pressure ($\sim 8 \text{ bar}$) [14].

While thermochemical ammonia decomposition ($2\text{NH}_3 \rightarrow \text{N}_2 + 3\text{H}_2$) using heterogeneous catalysts such as ruthenium is well established, required reaction temperature for high conversion above 90% is still very high [15], above 500°C , and even highly active catalysts result in a trace amount of ammonia in the product stream which is detrimental to a proton exchange membrane fuel cell (PEMFC). Therefore, such fuel conversion process requires a hydrogen purification step to be used in conjunction with a fuel cell. To address these issues, few studies have proposed a catalytic membrane reactor to both increase ammonia conversion while decreasing reaction temperature [16–19]. However, previous studies mostly utilize membranes on a porous support (palladium or silica on alumina), which still requires an additional purification unit due to a finite selectivity that strongly depends on the operation schemes such as reactant feed rate, reaction temperature, and sweep gas flowrates, or requires a thick Pd layer to allow high selectivity. Considering that the performance of PEMFC degrades even with ammonia concentration as low as 13 ppm [20] under 1 h of operation, membranes with porous supports can only be utilized for on-site NH_3 decomposition in conjunction with PEMFC if they can substantially reduce NH_3 concentration to the level harmless to PEMFC.

While hydrogen permeable palladium (Pd) membranes on porous supports are intensively developed, the main hurdle lies on the trade-offs between thickness (or cost) reduction and hydrogen selectivity (or purity). A compilation of thickness and selectivity data of hydrogen permeable membranes in the literature [21] suggests that thickness reductions accompany selectivity decreases, because it gets difficult to make faultless membranes as thickness becomes lower. On the other hand, group V body-centered-cubic (BCC) metals with a thin catalytic Pd layer below $1 \mu\text{m}$ are catching on due to high hydrogen permeability and near-infinite selectivity, resulting in over 99.9999% pure hydrogen [22,23]. Major problems of such Pd/BCC composite membranes have been considered to be the hydrogen embrittlement and durability issues; embrittlement issues are known to get worse with lower temperature resulting in higher hydrogen solubility in the metal, and durability issues are more apparent with higher temperature due to intermetallic diffusion of composite metals and morphological changes of the Pd layer. Recent publications demonstrate that those issues can be avoided by tailoring operating conditions [24,25], which suggest that there is a window of operation range where both problems can be minimized. Therefore, Pd/BCC composite membranes, when coupled with appropriate dehydrogenation reactions, can improve dehydrogenation conversion and directly produce fuel-cell grade high purity hydrogen. While required purification step of hydrogen can be removed, dehydrogenation reaction at elevated pressure (i.e. driving force of membrane separation) also allows a smaller reactor design, leading to a compact on-site power generation.

In this work, ammonia dehydrogenation is carried out with a fabricated Pd ($\sim 0.4 \mu\text{m}$)/Ta ($\sim 250 \mu\text{m}$) composite membrane and

synthesized Ru/La(10)- Al_2O_3 pellet catalysts packed in a tubular membrane reactor. Performance of as-fabricated membrane and catalyst is first evaluated in separate, and optimal operating conditions for coupling of NH_3 decomposition and H_2 separation using a Pd/BCC membrane are suggested. Various performance metrics of the membrane reactor, e.g. ammonia conversion, H_2 flux, recovery yield, and purity of separated H_2 are evaluated at a combination of varying temperature, pressure, space velocity, and sweep gas flow rates. Then, performance of a Pd/Ta membrane reactor is analyzed by operation at an optimized operation condition for an extended period of time. Finally, a potential on-site powering application of the coupled catalytic membrane reactor module is demonstrated by feeding as-separated H_2 directly, without any purification device, to PEMFC.

2. Experimental methods

2.1. Fabrication of membranes and catalysts

For composite membrane fabrication, Ta tubes ($> 99.95\%$; Koralco) with an outer diameter of 6.35 mm and total length of 125 mm with a wall thickness of 0.25 mm were utilized, yielding active permeation area of 25.2 cm^2 . Basic cleaning solution was prepared by dissolving $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ (98–102%, Alfa Aesar), Na_2CO_3 ($> 99.0\%$, Sigma-Aldrich), and NaOH (98%, Daejung Chemicals) in deionized (DI) water, and acidic cleaning solutions were 1 M and 10 M hydrochloric acids (Daejung Chemicals) and phosphoric acid (Daejung Chemicals). After the surface treatment, electroless deposition of Pd on Ta was carried out following a process established by Ma et al. [26] where detailed procedure is presented. An activation solution was SnCl_2 (Sigma-Aldrich) and PdCl_2 (Sigma-Aldrich) dissolved in DI water, and the plating solution was tetraammine palladium(II) chloride monohydrate (Pd (NH_3) $_4\text{Cl}_2 \cdot \text{H}_2\text{O}$) dissolved in ammonia (Samchun Chemical) with ethylenediaminetetraacetic acid disodium salt dehydrate (EDTA, Sigma-Aldrich). Thickness of the Pd on Ta was controlled by the duration of the plating. Finally before the permeation test, the membrane was heat-treated for 2 h at 500°C under N_2 condition for better adhesion of a Pd layer on Ta surface. For catalyst synthesis, lanthanum was doped on γ -alumina pellets (Alfa Aesar) by immersing them in $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (97%, Crown Guaranteed Reagents) solution followed by a calcination procedure as described in Chung et al. [27]. Then ruthenium ions were deposited on the La-doped pellet supports by a wet impregnation method described in Kathiraser et al. [28], where supports are immersed in a $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ (Sigma Aldrich) solution followed by a drying in a vacuum oven.

2.2. Characterization of Pd/Ta membranes and Ru/La(10)- Al_2O_3 catalysts

The samples were analyzed by using X-ray diffraction (XRD; D8 Discover with GADDS, Bruker), scanning electron microscopy (SEM; Inspect F50, FEI), transmission electron microscopy (TEM; Talos F200X, FEI), and high-angle annular dark-field scanning transmission electron microscopy (HAFFD-STEM) with energy dispersive X-ray (EDX). For XRD peak analyses of the membrane sample, Joint Committee on Powder Diffraction Standards (JCPDS) No. 46–1043 and 04–0788 were utilized for Pd and Ta, respectively.

2.3. Energy conversion process by ammonia dehydrogenation

Pure ammonia (NH_3 , 99.9995%), hydrogen (H_2 , 99.9995%), nitrogen (N_2 , 99.9995%) gases were purchased from Sinyang Oxygen Company Limited. Mass flow controller (MFC; F-201CB, Bronkhorst) units were used to control the flowrates of the gas streams going into the reactor as shown in Fig. 1a. Ammonia dehydrogenation was carried out in a double pipe reactor configuration (Fig. 1c) where outside shell is a stainless steel tube and the inside is whether a Pd/Ta composite membrane (for CMR experiments) or a dummy stainless steel tube (for

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