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Hydrogen generation from nanoflower platinum films



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ABSTRACT

For the first time with this study, flexible thin film platinum catalysts with nanoflower morphology to produce hydrogen gas from chemical hydrides have been introduced. We are also reporting a novel strategy for preparing hydrogen generation catalysts. This has been achieved by dealloying of aluminum from alloys of platinum and aluminum. The efforts in tailoring the catalyst morphology have resulted with very high catalytically active surface area of $119.8 \text{ m}^2 \text{ g}^{-1}$ catalyst system. Hence, the catalyst system in this study shows the highest rate in the literature in terms of any definition of hydrogen generation rate. The platinum loading of the films was only about $44.0 \mu\text{g cm}^{-2}$. Therefore, using very small amount of catalysts with very high activity greatly helps to overcome the challenges associated with the price of the precious catalysts. Moreover, considerable amount of flexibility has been provided when catalysts are prepared on Teflon™ and asymmetric polymeric membranes.

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Introduction

Hydrogen is one of the most promising future clean energy carriers since it provides zero-emission energy. One barrier to the widespread usage of hydrogen as a transportation fuel is its safe, efficient and inexpensive on-board storage, which is a combination currently lacking in conventional hydrogen storage technologies including cryogenic and high-pressure vessels. Chemical hydrides hold great promise in this respect due to their capacity to store hydrogen as a solid [1]. Among the chemical hydrides, boron hydrides have the largest volumetric and mass hydrogen densities [2]. The two major methods to produce hydrogen from a chemical hydride

are hydrolysis and thermolysis. Since hydrolysis has very slow kinetics, catalytic hydrolysis can be used to achieve higher production rates. Previously reported works on hydrogen generation from chemical hydrides always used very small systems and so they produced a limited amount of hydrogen [3–6]. In contrast, in this study the usage of novel catalyst morphologies to yield the highest possible hydrogen generation kinetics is presented. An effective hydrolysis reaction occurs only when chemical hydrides are in contact with a certain catalyst. Ruthenium (Ru), platinum (Pt), nickel (Ni), palladium (Pd), cobalt (Co), Ni–B, Co–B, Co–P, Ni–Co–B, carbon nanotubes (CNT) and graphene are examples of these catalysts [4–11]. Moreover, platinum supported on carbon (Pt/

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C), which are extensively utilized in Proton Exchange Membrane Fuel Cells (PEMFC's), are also appropriate for hydrogen gas generation [12]. Precious metal catalysts are costly while metal and alloy catalysts from iron, nickel and cobalt are more inexpensive. Therefore, researchers have been trying to replace precious metal catalysts with inexpensive materials to make hydrogen generation less costly. On the other hand, the hydrogen gas generation rate measurement is a very important issue in these catalytic systems. Interestingly, the hydrogen generation rate has been reported in several different ways. One of these ways is to report volume or moles of hydrogen per unit experimental time as ml min^{-1} , L h^{-1} , L day^{-1} , $\text{m}^3 \text{h}^{-1} \text{mol min}^{-1}$ etc. during hydrogen generation [4–18]. The other is in-situ measurement of hydrogen mass flow rates possibly by using a mass flow meter. However, for most of the studies, the reported hydrogen generation rate is normalized by the grams of catalyst and reported as $\text{L min}^{-1} \text{g}^{-1}_{\text{catalyst}}$ or $\text{mol min}^{-1} \text{g}^{-1}_{\text{catalyst}}$. However, this is not a robust way to express the catalytic activity since the catalytic activity is a function of the active surface area which is related to but not directly proportional to the amount of catalyst [18].

The performance of a catalyst for hydrogen generation may be better defined by several criteria. These are efficiency, stability and recovery of the catalysts. Therefore, highly stable and kinetically favorable catalysts are extremely preferable. In the area of hydrogen generation, any catalyst usually works kinetically faster for their initial runs. Then the hydrogen generation rate either stabilize and set to a lower value or the catalytic activity is worsen and even halted most probably due to the decomposition of the catalyst into other chemicals [7,19,20]. The latter is generally more expected for the non-nobel catalysts. Therefore, non-nobel catalysts cannot tolerate continues operation and significantly degrades their performance.

In the presence of the precious metal catalysts, stability and efficiency are always better than any other systems. However the price of the catalysts bring with the consideration of the limitations for their extensive usage. Particularly, there is a trade off between the performance and the cost of the system. Therefore, they usually utilized in very small systems. If, however, a very less amount of precious metal with very high surface area is achieved, then the price of the catalysts could becomes no longer a big issue. There have been lots of studies especially concentrated on heterogeneous precious catalysts. They can be either adsorbed on substrates such as carbon, graphite and carbon nanotubes, or we can see these catalysts as a layer deposited on the foamed substrates which is generally made of nickel. Non-precious catalysts are generally made of iron, and cobalt and nickel. The maximum hydrogen generation rate could be possible in the range of 0.01 and 27.0 L min^{-1} (or 5.0 and $130 \text{ L min}^{-1} \text{g}_{\text{catalyst}}$) for the precious catalyst. On the other hand, it was between 0.005 and 7.0 L min^{-1} (or 0.1 and $15.0 \text{ L min}^{-1} \text{g}_{\text{catalyst}}$) when the non-precious catalysts were used [7,10,21–25].

The form of the catalyst is another important issue. Film and powder forms are the most usual ones. However, the major disadvantages of using powder is that the difficulty of the separation of the catalyst from the by products of the reaction. Moreover, the control of the hydrogen generation rate is difficult and mixing of the catalyst in the solution for better

interaction is generally required. On the other hand, catalyst in the form of thin films, which has an extra degree of freedom to change the surface structure and surface morphology, can easily be recovered. Additionally, catalyst aggregation, which deteriorates the catalytic activity, has been prevented with the thin film catalyst. Therefore, for the first time with this study, we introduce flexible thin film platinum catalysts with nano-flower morphology to achieve high performance hydrogen generation.

Experimental

Materials

Hydrochloric acid (37 wt %) was purchased from Sigma Aldrich. Teflon™ substrate was provided from Oz-Ka Metal Inc. Teflon™ and asymmetric membranes were cleaned with acetone and deionized water, respectively. Then both substrates were dried under vacuum (1.0 mmHg) at 25 °C for overnight. Platinum and aluminum targets (99.99 wt %) were provided from Plus Materials. NaBH_4 (98.0 wt %) was purchased from Sigma Aldrich and used as received. In all experiments deionized water with the resistivity of $18.2 \text{ M } \Omega \text{ cm}$ (ELGA Purelab Option-Q) was used.

For the synthesis of copolymer used to prepare asymmetric membranes, acrylonitrile (AN, 99%) and 2-ethyl hexylacrylate (2EHA, 98%) (both supplied from Aldrich) were purified by vacuum distillation immediately before to use. Water soluble initiator, ammonium persulfate (APS, 99+%), iso-propyl alcohol (IPA), and sulfuric acid (all supplied from Acros Organics), which are technically pure, were used as received. The 1-dodecanthiol (Merck) is preferred as a chain transfer agent. DOWFAX 8390 solution surfactant was used as received. Magnesium sulfate (97% anhydrous), N,N-dimethyl formamide (DMF) (99.8%) and 1-methyl-2-pyrrolidone (NMP) (99%) were provided from Acros Organics and used as received.

Asymmetric membrane preparation

Asymmetric membranes were prepared according to following procedure [26]. The ingredients were mixed in a 250-mL three necked flask, which fitted with a condenser, glass stirrer, dropping funnel, nitrogen inlet tube, and thermocouple probe was charged with water; water, surfactant, initiator (65% of total initiator), mercaptan, and monomer mixture (20% of total monomer). Before mixing ingredients, the temperature was raised to 68 °C and the flask was purged with nitrogen for an hour. The remaining monomer mixture was added over a period of 2 h and 30 min. After addition of monomer mixture, the remaining initiator was poured through the dropping funnel. The latex was held at 68 °C for additional 45 min. The product was precipitated with 10% aqueous MgSO_4 solution and the copolymer was washed with distilled water for several times and then vacuum dried at 60 °C for overnight. Next, approximately 1.1 g of polyacrylonitrile-co-poly (2-ethyl hexylacrylate) (PAN(92)-co-P2EHA(8)) copolymer (intrinsic viscosity of 1.2 dL g^{-1}) was dissolved in 8.0 g of DMF. Then polymer mixture was poured

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