Hydrogen Generation by Hydrolysis of Sodium Borohydride Solutions

Sodium Borohydride를 이용한 수소 생산

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Introduction

Proton exchange membrane fuel cells (PEMFC) using hydrogen are on the verge of commercialization and expected to replace the internal combustion engine in transportation as well as residential power generation [1, 2]. However, efficient operation of the PEMFC needs hydrogen in pure form. Though hydrogen is mainly produced from the reformation of hydrocarbon feed stocks, the efficiency of the fuel cell is affected due to the presence of carbon monoxide. Moreover, low cost, safe hydrogen storage technologies are yet to be developed.

In view of the above, on site hydrogen production from the chemical hydrides is attractive, since the hydrogen will be purer without any fuel cell poisons [3-5]. Among the hydrides, sodium borohydride is desirable due to its high hydrogen storage capacity and the excellent stability of its alkaline solutions [6]. Schlesinger et. al [7] have reported that the alkaline borohydride solutions undergo hydrolysis in presence of various transition-metal catalysts to produce hydrogen. Based on this, various catalyst systems have been developed for hydrogen production from borohydride solutions and reported in recent years [8-10].

The application of Pt-alloy catalysts for the hydrolysis of sodium borohydride will be presented in this paper. The ion exchange resin dispersed as well as Lithium Cobalt Oxide ($LiCoO_2$) supported catalysts of Pt, Ru as well as alloy were prepared and tested for their efficiency to hydrogen production. The effect of catalyst support material as well as the sodium borohydride concentration on the hydrogen production rate will be presented.

Experimental

Catalysts Preparation

The Ruthenium precursor, $RuCl_3$ and Platinum precursor H_2PtCl_6 were used for the catalyst preparation. The ion exchange resin dispersed as well as the Lithium Cobalt Oxide ($LiCoO_2$) supported catalysts were prepared by the impregnation method. The catalysts were characterized by XRD and TEM. The composition of the ion exchange resin dispersed catalysts were determined by the ICP analysis.

Hydrogen generation experiments.

In a typical hydrogen generation experiment, 25ml of the Borohydride solution was taken in a thermostated tubular glass vessel. The catalyst template in a titanium mesh pouch was tied over a stainless steel rod and immersed into the solution through a rubber septum. A thermocouple was also inserted through the septum to measure the temperature. The hydrogen flow was measured using a mass flow meter.

Results and discussion

The rate of hydrogen generation for various catalysts is given in Fig 1. It can be seen from the figure that the hydrogen generation rate on the $LiCoO_2$ oxide supported catalysts is higher than that of the ion exchange resin dispersed catalysts. The higher efficiency of oxide supported catalysts is reported to be due to the adsorption of water on the surface of the oxide. The H^- from BH_4^- discharges electron through the catalyst which reduces H^+ from water to generate hydrogen[10].

The hydrogen generation rate with PtRu-$LiCoO_2$ is almost double of that obtained with Pt-$LiCoO_2$ and Ru-$LiCoO_2$ catalysts. The cumulative hydrogen generation rate with different catalysts is given in Fig.2. The total volume of hydrogen present in 25ml of the 5%$NaBH_4$ (5%NaOH) solution was found to be 3.333litres. The total volume of hydrogen generated with time is plotted in Fig.2.

With PtRu-$LiCoO_2$ as the catalyst, almost all the Borohydride hydrolyzed within 15 minutes. Where as, it took around 30-40minutes with Pt-$LiCoO_2$ and Ru-$LiCoO_2$ respectively. The cumulative hydrogen production rate of Pt-IRA 400 catalyst is also comparable with Pt-$LiCoO_2$ and Ru-$LiCoO_2$ catalysts. But the hydrogen production rate was only around 50% in 45 minutes with Ru-IRA 400 resin supported catalyst.

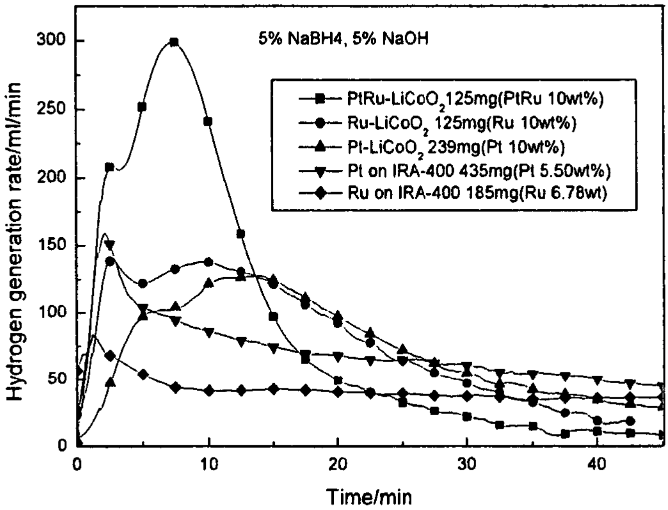

Fig. 1 Hydrogen generation with different catalysts

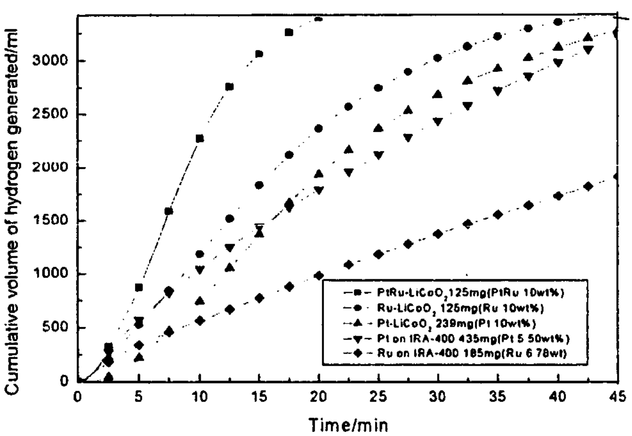

Fig.2 The cumulative hydrogen generation rate with different catalysts

Conclusions

The $LiCoO_2$ supported catalysts behave better than ion exchange resin dispersed catalysts for the hydrolysis of borohydride solutions. The efficiency of PtRu-$LiCoO_2$ is almost double than that of either Ru-$LiCoO_2$ or Pt-$LiCoO_2$. The superior performance of PtRu-$LiCoO_2$ catalyst may be due to the enhanced adsorption characteristics coupled with the synergic effect of the oxide support.

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