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Hydrogen production by hydrolysis of sodium borohydride for PEM fuel cells feeding

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Abstract

In this work, hydrogen is produced by a hydrolysis process that uses sodium borohydride as a hydrogen carrier and storage media. High purity hydrogen is obtained at low temperatures with high volumetric and gravimetric storage efficiencies; reaction products are non-toxic. The produced hydrogen can be supply on-demand at specified flow by tailor made developed catalyst. Hydrogen feeding to a low power fuel cell was accomplished. According to experimental conditions conversion rates of 100% are possible. Catalyst is demonstrated to be reusable.

Keywords: Chemical hydrides, sodium borohydride, production of hydrogen, fuel cells

1 Introduction

A major challenge facing our planet today relates to the problem of climate change and its links to global society's present and future energy needs. Hydrogen and fuel cells are now widely regarded as key energy solutions for the 21st century. These technologies will contribute significantly to a reduction in environmental impact, enhanced energy security (and diversity) and the creation of new energy industries.

However, the transition from an energy system with fossil fuel to a hydrogen-based economy involves significant scientific, technological and socioeconomic barriers to the implementation of hydrogen and fuel cells as the clean energy technologies of the future. Hydrogen production and storage continue to be major technological barriers.

Energy densities, cost, safety and ease of manufacture, are amongst the factors to be taken into account for the evaluation of storage systems.

Chemical hydrides, particularly borohydrides, are currently being developed as storage options, since they exhibit good energy densities. Cost effective recycling methods are needed for improvement of this option for use in selected fuel cell applications. Sodium borohydride (NaBH₄) was chosen due to its high hydrogen content (10.6 wt.%), good storability in alkaline solution, easy control of hydrogen generation rates, moderate operation temperature and environmentally benign hydrolysis product [1-3].

NaBH₄ reacts exothermally with water, but the reaction rate diminishes with time as the production of NaBO₂ makes the solution alkaline.

Catalysts are essential for a controlled constant hydrogen production rate.

 $NaBH_4 + (2+x) H_2O \rightarrow NaBO_2.x H_2O + 4H_2\uparrow (-218 \text{ kJmol}^{-1}) (1)$

In this work, sodium borohydride is the option taken for production on-demand hydrogen for an application involving the feeding of a low power fuel cell, which may require hydrogen at a rate of 1 Lmin⁻¹.

2 Experimental and Results

The selected catalyst, apart from appropriate catalytic activity and suitable kinetics, face issues of durability (lifetime) and stability of reaction rates (re-use) with time, in aggressive environment conditions - highly alkaline solutions with violent



exothermic hydrogen evolution. Available water fraction and the effect of by-products have to be accounted for.

Bimetallic nickel based catalyst have been developed in order to comply with the target to feed a low power fuel cell that may require hydrogen at a rate of 1 Lmin⁻¹. Table 1 shows obtained rates in repeated utilizations of the developed catalyst. Tests were conducted in a small batch reactor.

Table 1. Hydrogen production rates after re-use of the developed catalysts for sodium borohydride

Catalyst		Solution Concentration (wt%)	Temperature (ºC)	H2 Production Rate (L min ⁻¹ g ⁻¹)
Ni-bi I	1ª Utilization	10% NaBH₄; 7% NaOH	25 (initial) without temperature control	0.38
	11 ^a Utilization			0.67
Ni-bi II	1 ^a Utilization			4.50
	6 ^a Utilization			14.17

hydrolysis.

To design a hydrogen generator, hydrogen generation rates were measured using the catalyst as a function of solution temperature, amount of catalyst loading, $NaBH_4$ concentration, and NaOH (as stabilizer) concentration [4-6],

A PEM fuel cell of 5 W nominal power was selected, for an application. Laboratory test were conducted using a glass reactor in a laboratory setup shown in figure 1a), for on-demand hydrogen use. The reactor can be refilled at any time with borohydride solution or solid borohydride in the form of caplets. Catalyst can be re-used.

Figure 1b) compares the polarization curve of the fuel cell obtained using hydrogen produced by borohydride and compressed hydrogen (CH2) from a gas bottle. Power curves as a function of the generated current are also shown. Stability of the potential of the fuel cell for a current demand of 1 and 2 A was demonstrated.

Some laboratory tests involved the production of hydrogen under pressure, using a 0.220 L stainless steel reactor. A typical gas production rate of 206 mbarmin⁻¹ was achieved, which was compatible with the application [6].

Issues related with water and temperature management are being studied in order to scale-up the application for a 50 W fuel cell.

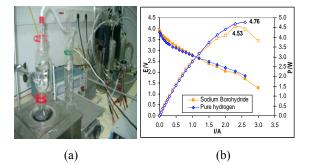


Fig.1 Experimental set-up of the hydrogen production and feeding system for a 5 W fuel cell (a); Comparison between polarization curves with hydrogen from sodium borohydride (10 wt% aqueous solution, stabilised with 3 wt% NaOH) and from hydrogen from a gas bottle through a PEM testing station (0.2 L.min⁻¹, 0.3 bar; 22°C).

References

[1] Z.P. Li, B.H. Liu, K. Arai, K. Asaba, S. Suda, Evaluation of alkaline borohydride solutions as the fuel for fuel cell, J.P. Sources 126 (2004) 28-33.

[2] J.-H. Kim, H. Lee, S.-C. Han, H.-S. Kim, M.-S. Song, J.-Y. Lee, Production of hydrogen from sodium borohydride in alkaline solution: development of catalyst with high performance, Int. J. Hydrogen Energy 29 (2004) 263-267.

[3] R. K. Raman, A. K. Shukla, A Direct Borohydride/Hydrogen Peroxide Fuel Cell with Reduced Alkali Crossover, Fuel Cells 7 (2007) 225-231.

[4] A.M.F.R. Pinto, D.S. Falcão, R.A. Silva and C.M. Rangel, Hydrogen generation and storage from hydrolysis of sodium borohydride in batch reactors. Int. J. Hydrogen Energy 31 (2006) 1341-1347.

[5] C.M. Rangel, R.A. Silva, V.R. Fernandes. Hydrogen storage and production at low temperatures from borohydrides. 16th World Conference on Hydrogen Energy, paper 598, Lyon, 2006.

[6] C.M Rangel, R.A. Silva, A.M.F.R. Pinto, "Fuel Cell and on-Demand Hydrogen Production: Didactic Demonstration Prototype" International Conference in Power Engineering, Energy and Electric Drives, Setúbal, 2007.