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# Poisoning-tolerant metal hydride materials and their application for hydrogen separation from CO<sub>2</sub>/CO containing gas mixtures

K.D. Modibane, M. Williams, M. Lototskyy\*, M.W. Davids, Ye. Klochko, B.G. Pollet

HySA Systems Competence Centre, South African Institute for Advanced Materials Chemistry, University of the Western Cape, Private Bag X17, Bellville 7535, South Africa

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## ABSTRACT

Metal hydride materials offer attractive solutions in addressing problems associated with hydrogen separation and purification from waste flue gases. However, a challenging problem is the deterioration of hydrogen charging performances resulting from the surface chemical action of electrophilic gases. In this work, the feasibility study of poisoning tolerance of surface modified AB<sub>5</sub>-type hydride forming materials and their application for hydrogen separation from process gases containing carbon dioxide and monoxide was carried out. Target composition of La(Ni,Co,Mn,Al)<sub>5</sub> substrate was chosen to provide maximum reversible hydrogen capacity at the process conditions. The selected substrate alloy has been shown to be effectively surface-modified by fluorination followed by electrodeless deposition of palladium. The surface-modified material exhibited good coating quality, high cycle stability and minimal deterioration of kinetics of selective hydrogen absorption at room temperature, from gas mixtures containing 10% CO<sub>2</sub> and up to 100 ppm CO. The experimental prototype of a hydrogen separation unit, based on the surface-modified metal hydride material, was tested and exhibited stable hydrogen separation and purification performances when exposed to feedstocks containing concentrations of CO<sub>2</sub> and CO of up to 30% and 100 ppm, respectively.

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## 1. Introduction

Metal hydride (MH) materials have found a number of promising gas-phase applications in processes of considerable economic potential, such as hydrogen storage, separation and recovery, thermally-driven compressors and heat pumps, etc. [1–3]. These materials exhibit a favourable combination of their properties, including reversibility and selectivity of interaction with H<sub>2</sub> gas at mild conditions, high volumetric

density of hydrogen in the solid, significant heat effects in the course of hydrogenation/dehydrogenation. Thus they are very flexible in the applications, and often allow to develop multi-functional facilities (e.g., for hydrogen storage, purification and controlled supply) which offer to an end-user safe, efficient and cost-saving solutions [4].

A number of process developments utilising MH for separation and purification of hydrogen were undertaken since 1970th [5–15]. Mainly, the solutions [8,9,13,14], use AB<sub>5</sub>-type

\* Corresponding author. Tel.: +27 21 9599314; fax: +27 21 9599312.

E-mail addresses: [mlototskyy@uwc.ac.za](mailto:mlototskyy@uwc.ac.za), [mvlot@hysasystems.org](mailto:mvlot@hysasystems.org) (M. Lototskyy).

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hydrogen storage intermetallics to extract H<sub>2</sub> from process gases typical for production of ammonia (N<sub>2</sub>, Ar, hydrocarbons and NH<sub>3</sub> impurities; up to 50% in total); the process conditions cover temperature range from 20 to 150 °C and pressures 10–100 bar H<sub>2</sub>. Some of these developments were implemented on industrial-scale [9,14]. Feasibility studies of application of MH for hydrogen extraction from gas mixtures containing CO<sub>2</sub> and CO were also reported, and the suitable solutions were suggested [5,7,16,17].

The H absorption process often requires higher temperatures and, correspondingly, usage of hydride-forming materials characterised by higher hydride stabilities: LaNi<sub>4</sub>Cu [5], Ti-based alloys and composites [7,16], activated Mg [12], or Pd alloy [15]. At the same time, a challenging problem that hampers application of MH for hydrogen separation from the mixtures containing chemically-aggressive gases (O<sub>2</sub>, H<sub>2</sub>O, CO, sulphur-containing compounds, etc.) is the deterioration of MH performances as a result of the presence in hydrogen of gas impurities [3,18] able to easily react with MH surfaces resulting in the formation of surface compounds (oxides and hydroxides, carbonyls, sulphides) which seriously limit hydrogen absorption. Most probably, the impurities deactivate surface centres responsible for H<sub>2</sub> dissociation (e.g., Ni clusters for AB<sub>5</sub>-type alloys) resulting in the retardation of this process, which represents the rate-limiting step in hydrogen absorption [19,20].

So far, two approaches were implemented to address the above-mentioned problem. The first one includes removal of the impurities prior to H absorption in the MH [17] while the second improves the poisoning tolerance of MH by their surface modification [20–23].

In our previous studies [24–28] we investigated the influence of surface modification (by fluorination and/or electrodeless deposition of metals, including Pd) of AB<sub>5</sub>-type alloys on their activation performances and poisoning tolerance. The corresponding surface modification procedures for the preparation of the advanced materials were developed [29,30], and feasibility of their application for hydrogen purification from (CO<sub>2</sub> + CO)-containing gases was demonstrated [31,32]. The novel features of the developed surface modification procedures include (i) enhancement of PGM deposition by surface functionalisation of the metallic hydride-forming material [25,28,29], and (ii) combination of fluorination and enhanced PGM deposition procedures [24,28,30].

This investigation presents further feasibility study of hydrogen absorption from mixed gas feedstocks, by unmodified and surface-modified (using the fluorination – Pd encapsulation technique) La(Ni,Mn,Al,Co)<sub>5</sub> alloy, which was subsequently utilised for testing of a prototype hydrogen extraction and purification system.

## 2. Experimental

The AB<sub>5</sub>-type substrates were initially arc-melted at the Institute for Energy Technology (IFE) using high-purity starting materials, annealed for 72 h at 1000 °C in vacuum, and crushed in a mortar. Quantities of the AB<sub>5</sub> materials for

prototyping applications were purchased from Guangzhou Research Institute of Non-Ferrous Metals.

Surface modification of the substrate material was conducted through fluorination and followed by autocatalytic deposition of Pd at the South African Institute for Advanced Materials Chemistry (SAIAMC). The rationale behind this approach was the combination of the large increase in the specific surface area of the material with fluorination, and the enhanced activation kinetics observed with deposition of Pd catalytic layers, to form materials with exquisite hydrogen sorption properties. The fluorination and autocatalytic deposition of Pd were applied to ~300 g batch of the La(Ni,Co,Al,Mn)<sub>5</sub> substrate. Further details on the surface modification procedure and characterisation (including activation performances) of the surface-modified materials can be found elsewhere [21,24,28,30,32].

The hydrogen absorption/desorption performances (PCT diagrams) of several substrate alloys were measured using a PCT Pro-2000 gas sorption analyzer (Hy-Energy LLC) at T = 50–200 °C and P<sub>H<sub>2</sub></sub> = 0–50 bar H<sub>2</sub>. The raw PCT data were pre-processed using macros HyDataAnalysis Version 2.2.3, © Hy-Energy 2007 supplied as auxiliary software together with the instrument, in the environment IgorPro Version 6.0.3.1, © WaveMetrics Inc. The pre-processing, in particular, introduced correction into the calculation of amount of absorbed/desorbed hydrogen taking into account displacement volume. Further PCT data processing was done using the model of phase equilibria in metal–hydrogen systems reported by Lototsky et al. [33]. The absorption and desorption datasets were processed separately.

Kinetics of hydrogen absorption from pure H<sub>2</sub> and gas mixtures by MH material, in a running flow mode, was studied using procedures similar to one reported earlier [28,31]. The MH material (m ~ 4 g) was loaded in the running-flow tubular reactor (internal diameter – 10 mm). Activation of the MH sample and determination of amount of hydrogen absorbed from the feeding gas for the specified period of time was carried out using a Sieverts-type installation. The experiments were carried out as follows: after activation (3 cycles of 1-h vacuum heating to 200 °C followed by absorption of pure H<sub>2</sub> at room temperature), the sample was evacuated at 200 °C for 1 h and cooled to the operational temperature (20 °C). The sample was exposed to the flow of the feeding gas at the constant flow rate (0.25 and 1 L/min STP for pure H<sub>2</sub> and gas mixture containing 25% H<sub>2</sub>, respectively) and pressure (2.0 bar for pure H<sub>2</sub>, 8.0 bar for the mixture), for the specified period (1–30 min). Hydrogen absorption rates, *r*, in the running-flow mode were estimated using simplified thermal calculations according to the formula<sup>1</sup>:

$$r = C_H \frac{\Delta T}{\int_0^{t_{MAX}} \Delta T d\tau} \quad (1)$$

where  $\Delta T$  is the difference between actual (*T*) and starting (*T*<sub>0</sub>) sample temperature,  $\tau$  is time.

<sup>1</sup> The applicability of the simplified eqn. (1) at the applied operation conditions was shown in our previous work [32].

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