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The catalytic effect of Nb_2O_5 on the electrochemical hydrogenation of nanocrystalline magnesium

D. Zander[a,*], L. Lyubenova[a], U. Köster[a], M. Dornheim[b], F. Aguey-Zinsou[b], T. Klassen[b]

[a] Department of Biochemical and Chemical Engineering, University of Dortmund, D-44221 Dortmund, Germany
[b] Institute for Materials Research, GKSS Research Centre, D-21502 Geesthacht, Germany

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Abstract

Nanocrystalline Mg powder without and with 2 mol% Nb_2O_5 catalyst was studied in a 6 M KOH electrolyte as electrode material for electrochemical hydrogen charging processes. Since the hydrogen overpotential of Mg, which is a measure of the hydrogen evolution at the electrode surface, was observed to be reduced by the addition of Nb_2O_5, it is assumed that the catalyst influences the electrode reactions. Considering this assumption hydrogenation was studied at different current densities. The storage capacity as well as the kinetic of Mg/Nb_2O_5 electrodes increased significantly up to 1 wt.% H_2 at a charging time of 30 min with decreasing current density. The storage capacity of nanocrystalline Mg powder showed only minor changes to lower hydrogen contents with decreasing current density.

Keywords: Magnesium; Nanocrystalline; Nb_2O_5; Catalyst; Electrochemical; Hydrogenation; Metal hydrides; Hydrogen storage

1. Introduction

Desirable properties of hydrogen storage materials include high hydrogen capacity, high number of hydrogenation/dehydrogenation cycles, low temperature of dissociation and microstructural stability. Hydrogen storage can proceed from the gas phase as well as during cathodic charging.

Whereas, bulk Mg cannot be used as hydrogen storage material due to the early formation of a Mg-hydride layer which acts as a hydrogen barrier, nanocrystalline Mg-based hydrides are considered to be an important candidate for safe energy storage and transportation [1]. But due to still high sorption temperatures and unknown cycling life commercialization in mobile storage systems, metal/hydride batteries and other clean applications have been slowed down [2,3].

Recently, it has been published that for hydrogenation from the gas phase the design of improved nanocrystalline Mg alloys can proceed by the addition of metal oxides, e.g. V_2O_5, Nb_2O_5 [4–7] as catalysts. Furthermore, these nanocrystalline Mg alloys exhibit very good cycling properties [4]. However, these studies have focused only on the hydriding characteristics of nanocrystalline Mg with the addition of metal oxides in the gas phase. In order to verify whether such an addition improves also electrochemical hydrogenation, nanocrystalline Mg powder without and with 2 mol% Nb_2O_5 catalyst as an electrode material for electrochemical hydrogen charging processes electrolyte was studied in a 6 M KOH [8]. This first investigation revealed a strong influence of the compaction parameters and the current density, but no influence of the catalyst on the hydrogenation behavior at high current densities. In addition it was reported that the addition of graphite and PTFE to the Mg/Nb_2O_5 electrodes improves the charging kinetic as well as the hydrogen content.

The aim of this paper is to present further results on the influence of Nb_2O_5 on electrochemical hydrogenation of nanocrystalline Mg in particular at current densities lower than 50 mA/g. The mechanisms by which metal oxides improve hydrogen absorption as well as desorption are still unclear and should be investigated also by electrochemical investigations in some detail.

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* Corresponding author.
E-mail addresses: daniela.zander@bci-dortmund.de, daniela.zander@bci.uni-dortmund.de (D. Zander).

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2. Experimental

Mg powder without and with 2 mol% Nb_2O_5 as a catalyst was prepared by milling MgH_2 (Goldschmidt AG, 95% purity-the rest being magnesium) using a planetary ball mill (Fritsch P5) with a ball to powder weight ratio of 400 g/40 g and subsequent desorption of the MgH_2 powders at 300 °C. Two molar percent Nb_2O_5 powder was added after milling MgH_2 for 20 h and blended by milling for additional 100 h. The powder was used to design a proper electrode for electrochemical hydrogenation which provides good mechanical stability and good conductivity to allow the dissociation and adsorption of hydrogen at the surface as well as diffusion into the material. The Mg electrodes were prepared by compaction at different pressures without any additions as well as with 5 wt.% graphite and 5 wt.% PTFE. Since Mg is highly reactive in oxygen the preparation of the powders, including milling and electrode preparation, was performed inside a glove box under a continuously purified Ar atmosphere. Cathodic hydrogenation was carried out in a 6 M KOH electrolyte at 25 °C and a current density between $i = 50$ mA/g and $i = 5$ mA/g. Further electrochemical measurements such as determining the overvoltage were perfomed under the same electrolyte conditions. The hydrogen content was measured by a hydrogen determinator (RH-404, Leco). Morphology and microstructure of the Mg powder with and without Nb_2O_5 were investigated by X-ray diffraction, SEM and TEM. To prevent the Mg powder from oxidation the TEM samples were dispersed in toluene in a glove box, dropped on a copper grid and inserted immediately in the TEM.

3. Results and discussion

Microstructural investigations by SEM (Fig. 1) and TEM (Fig. 2) of desorbed MgH_2 powders without and with 2 mol% Nb_2O_5 powder showed a Mg particle size of 5–10 μm. X-ray as well as electron diffraction of MgH_2 without and with catalyst after thermal desorption at 300 °C (Fig. 2c) revealed the precipitation of nanocrystalline MgH_2 within the Mg particles. The observed hydrogen content after thermal desorption was 0.15 wt.% H_2; this explains the existence of nanocrystalline MgH_2 particles as seen by TEM. The grain size of the Nb_2O_5 catalyst of Mg/Nb_2O_5 powder was found to be 50–200 nm.

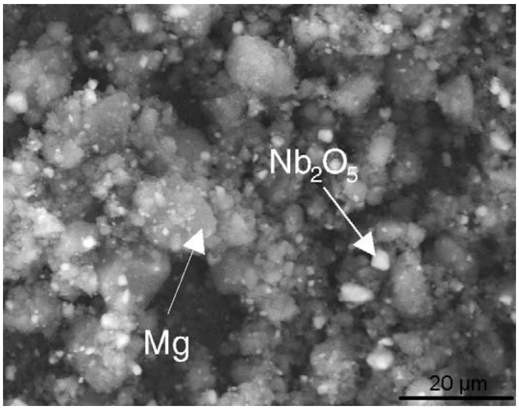

Fig. 1. Mg-powder with Nb_2O_5 catalyst (SEM micrograph).

The main electrode parameters influencing the cathodic charging are given by the compaction, the electrochemical surface reaction and the chosen catalyst. As reported earlier [8] during hydrogen charging of Mg and Mg/Nb_2O_5 electrodes a strong influence of the (1) compaction parameters and (2) the current density on the hydrogenation behavior but (3) no influence of the catalyst on the hydrogenation at a high current density of 50 mA/g, a charging time of 3 h at 25 °C and different porosities was observed. Recent results [5,6] on the influence of different Nb_2O_5 contents on the gaseous hydrogen reaction kinetics of nanocrystalline Mg showed that the catalytic effect of Nb_2O_5 is improved in absorption as well as desorption. Therefore, it was assumed that the observed influence of the current density on the Mg/Nb_2O_5 electrode and the independence of the addition of the catalyst on the hydrogenation indicate that the catalyst plays a major role regarding the electrochemical processes at the electrode surface. In order to reveal this assumption, the influence of the current density on Mg and Mg/Nb_2O_5 electrodes compacted with a suspension of graphite and PTFE at a compaction pressure of 6.2 N/mm^2 was studied (Fig. 3). A strong influence of

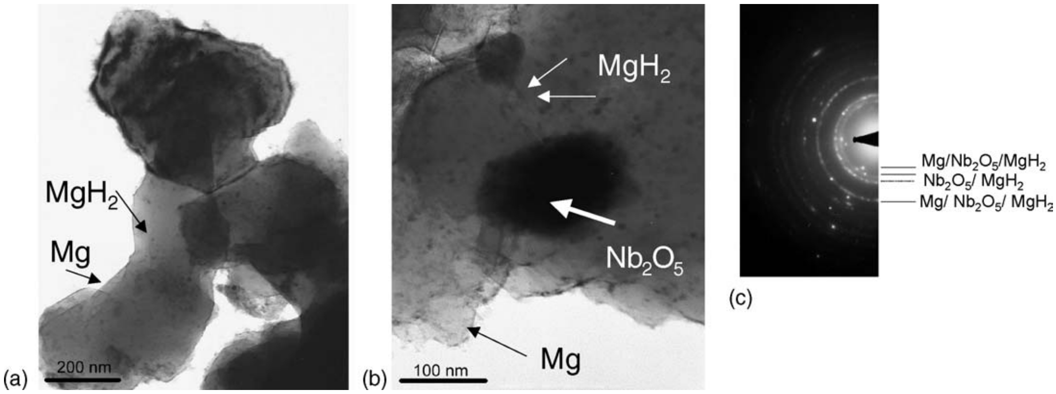

Fig. 2. Mg-powder (a) without and (b) with Nb_2O_5 catalyst (TEM micrographs) and (c) electron diffraction pattern of Mg-powder with Nb_2O_5 catalyst.

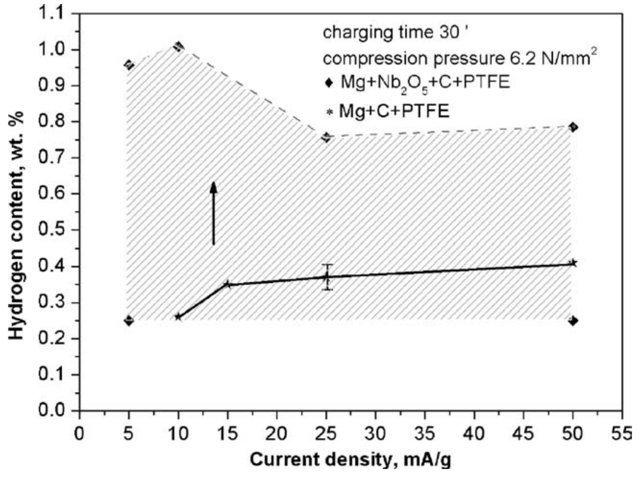

Fig. 3. Influence of the current density after charging for 30 min on Mg/Nb_2O_5-electrodes compacted with a suspension of graphite and PTFE at a compaction pressure of 6.2 N/mm^2.

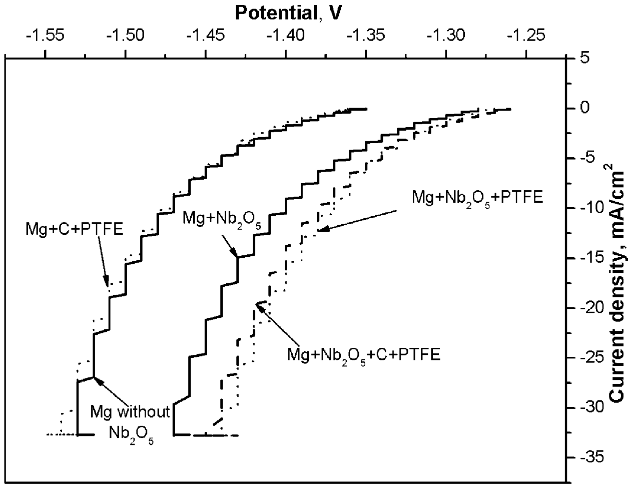

Fig. 4. Potentiodynamic polarization of the Mg and Mg/Nb_2O_5-electrodes without and with C/PTFE compacted with a pressure of 6.2 N/mm^2.

the catalyst was observed with decreasing current densities. The results for the Mg electrodes show a high accuracy in comparison to the broad scattering for the Mg/Nb_2O_5 electrodes (grey shaded area). The observed hydrogen contents scattered between 0.25 and 1.0 wt.% for the Mg/Nb_2O_5 electrodes. It is assumed that the catalyst distribution influences the upper limit and the scattering of the storage capacity as well as the oxidation process at the surface during preparation. However, a strong influence of the catalyst was observed with decreasing current densities for the upper hydrogen charging limit. While the storage capacity of about 0.4 wt.% H_2 of the Mg-electrode changes only minor to lower hydrogen contents of 0.35 wt.% with decreasing current density, the storage capacity as well as the kinetic of Mg/Nb_2O_5 electrodes increased significantly up to 1 wt.% H_2 at a charging time of 30 min with decreasing current density. Measurements at a limiting value of $i \leq 10$ mA/g, however, indicate a change of the electrochemical processes at the electrode surface.

Potentiodynamic polarization experiments (Fig. 4) gave some more information regarding the surface reactions at the electrode, specially regarding the hydrogen overvoltage of the investigated electrodes. Depending on the hydrogen overpotential and the current density three competing reactions can occur at the electrochemical surface:

$$H_3O^+ + e^- \rightarrow H_{ad} + H_2O \quad \text{Volmerreaction}$$

$$H_{ad} + H_{ad} \rightarrow H_2 \quad \text{Tafelreaction}$$

$$H_{ad} + H_3O^+ + e^- \rightarrow H_2 + H_2O \quad \text{Heyrowskireaction}$$

It was observed that Nb_2O_5 decreases the hydrogen overvoltage $\eta_{2.5}$ of Mg compacted at a compaction pressure of 6.2 N/mm^2. No significant influence of the addition of graphite as well as PTFE on the hydrogen overvoltage was observed. The reduced hydrogen overvoltage due to the catalyst is assumed to accelerate the hydrogen evolution at the electrode surface and explains the surprising independence of the addition of the catalyst on the hydrogen content as well as the charging kinetics at 50 mA/g and a charging time of 3 h. Earlier it was assumed that current densities of 50 mA/g lead to the preferred recombination of H_{ad} and a reduced adsorption of hydrogen [8]. At lower current densities (Fig. 3) it is assumed that the Volmer reaction $H_3O^+ + e^- \rightarrow H_{ad} + H_2O$ will become the speed limiting reaction and the competing Tafel reaction ($H_{ad} + H_{ad} \rightarrow H_2$) or Heyrowski reaction ($H_{ad} + H_3O^+ + e^- \rightarrow H_2 + H_2O$) will be irrelevant for the Mg/Nb_2O_5 electrodes. It is likely that due to the high hydrogen overvoltage of the Mg electrodes and the resulting oxidation at the surface the influence of the current density on the storage capacity becomes only minor. It is assumed that at very low current densities <10 mA/g the electrochemical equilibrium is moved to the anodic reaction and leads to a lower storage capacity of the Mg/Nb_2O_5 electrodes because of an increased oxidation in the 6 M KOH electrolyte. The electrochemical investigations showed the major influence of the Nb_2O_5 catalyst on the electrochemical surface reactions and therefore on the storage capacity as well as on the kinetics. Further microstructural and electrochemical investigations are underway and should clarify the effect of Nb_2O_5 on the charging behavior of nanocrystalline Mg in more detail.

4. Conclusion

Nanocrystalline Mg powder without and with 2 mol% Nb_2O_5 catalyst compacted with a suspension of graphite and PTFE at a compaction pressure of 6.2 N/mm^2 was studied in a 6 M KOH as an electrode material for electrochemical hydrogen charging processes electrolyte. A strong influence of the Nb_2O_5 catalyst on the electrochemical surface reaction was observed with decreasing current densities. Whereas, the change of the storage capacity of the Mg-electrode showed only minor changes to lower hydrogen contents. With decreasing current density the storage capacity as well as the kinetics of Mg/Nb_2O_5 electrodes increased significantly up to 1 wt.% H_2 at a charging time of 30 min with decreasing current density. The hydrogen overpotential of Mg is much higher than for Mg/Nb_2O_5. It is shown that the catalyst influences significantly the electrode reactions and the oxidation mechanism in the electrolyte.

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